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# THE GAMMA RADIOLYSIS OF AMMONIA AND THE METHYLAMINES IN THE GAS PHASE

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THE GAMMA RADIOLYSIS OF AMMONIA  
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BY

ROBERT CARL SCHIEK

B. S., Lowell Technological Institute, 1957

A THESIS

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This thesis has been examined and approved.

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Robert C. Schick

**To the Memory of my Father and Mother**

**1959**

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## INTRODUCTION

### A. Foreword

Chemical effects brought about by the absorption of ionizing radiation comprise the field of radiation chemistry. The primary interaction of radiation is with the orbital electrons of an atom or molecule producing ionization and excitation. The chemical reactions are initiated by these transient states of higher energy.

Investigation in this field may take two paths, (a) a study of elementary processes or (b) a study of the products from radiation induced reactions and of the mechanisms involved.

This thesis concerns itself with the radiolysis of ammonia and the methylamines and the mechanisms of product formation.

Previous work<sup>1</sup> in this laboratory was done on the gamma induced exchange of carbon-14 between labelled ethane and methylamine. While the radiolysis of ethane<sup>2</sup> has been studied, that of methylamine has not. Results of studies of the photolysis and thermal decomposition of the methylamines are available. A variety of products were identified, but the experiments were hampered with difficulties. Comparisons between these studies and the radiolysis can possibly be made to see if similar types of reactions are taking place.

Hart<sup>3a</sup> stated in his review in 1954, "Relatively few

chemical reactions produced by ionization processes in gases have been studied." Seven years later, Magee<sup>3e</sup> writes, "The elementary processes of the gas phase can be studied theoretically and experimentally with available techniques, and for this reason radiation chemistry of the gas phase may be the most profitable area for investigation. However, examination of the current literature indicates that very little gas phase work is in progress."

The importance of radiation chemistry and its practical applications were brought forth recently by two articles appearing in Chemical and Engineering News.<sup>4</sup> The production of ethyl bromide by use of a Cobalt 60 irradiator is the first commercial application. The production of hydrazine is a second possibility.

#### B. Radiation Interactions

Cobalt 60 is a gamma ray emitter. Two photons are emitted, one of 1.17 Mev. energy, the other of 1.33 Mev. energy. The main interaction of these photons with matter is by Compton scattering. This involves the interaction of a photon with an orbital electron in which a part of the photon's energy is transferred. This results in the photon being deflected from its path with lower energy and an ejected electron. The ejected electron has an energy spectrum from 0 to 1.04 Mev. These ejected electrons, Compton electrons, can also interact with atoms and molecules producing additional ionization and excitation. The average energy to produce an ion-pair in the gas phase is approximately 30 e.v. Thus, excess energy is

available.

The fundamental difference between irradiation of gases and condensed systems is that track effects have greater significance in the condensed phases. Beyond this, similar elementary processes and transient states exist in both.

The transient states can be grouped into three classes, ions, excited species and free radicals.

Positive ions result from removal of an electron or electron removal followed by bond rupture. Negative ions can also exist and are formed by electron capture. These ions can then enter into various types of interactions.

Ion-molecule reactions<sup>5</sup> are important. However, their occurrence is dependent, as are other reactions, upon successful competition with other reactions, including neutralization and molecular rearrangements.

Excited species may be produced initially by electrons or by neutralization. In the gas phase, excited states may parallel those found in photochemistry except that many more excited states can exist. Again the eventual fate of the excited specie, as in the case of the ions, depends upon competition with other reactions. Some of these are charge transfer, dissociation, deactivation by collision.

The third type of intermediates, free radicals, being products of the decomposition of excited species or the by-product of ion-molecule and neutralization reactions are more prevalent in condensed phases. Radical-radical reactions in

condensed phases are due to cage effects which are absent in the gas phase.

A recently published text by Lind<sup>6</sup> is a good source, covering both principles and experimental work. Recent literature and background in the field are reported in survey articles published in Annual Review of Physical Chemistry<sup>3</sup> and Annual Review of Nuclear Science.<sup>7</sup>

Allied fields such as photochemistry have much in common with radiation chemistry. Although there are differences, such fields may provide additional information.

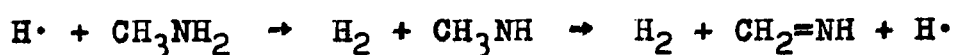
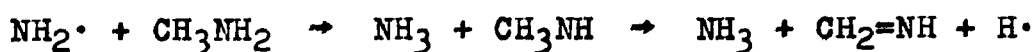
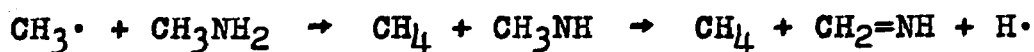
### C. History of Thermal and Photochemical Studies of the Methylamines

#### 1. Methylamine

Muller<sup>8</sup>, in 1886, decomposed methylamine at 1200°C. The products identified were ammonia, hydrogen cyanide, methane and hydrogen.

A photo decomposition study was done by Taylor and Emeléus<sup>9</sup> in 1931 with identification of hydrogen, methane ethane and nitrogen as gaseous products. An unidentified liquid was also produced.

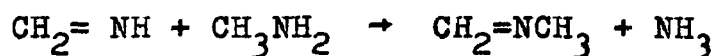
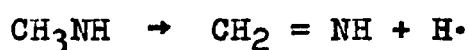
In 1935, Emeléus and Jolly<sup>10</sup> investigated the kinetics of the decomposition of methylamine at 540°C. to 560°C. and showed that the decomposition followed first-order kinetics. They proposed the following mechanism to explain the products hydrogen, hydrogen cyanide, methane and ammonia.



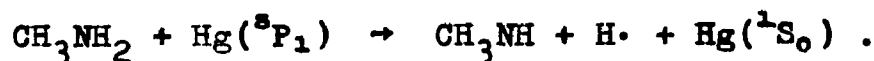
The same authors later studied the photochemical decomposition<sup>11</sup> at 100°C. and found as products hydrogen, ammonia and a brown liquid. They postulated two intermediates,  $\text{CH}_3\text{N}=\text{CH}_2$ , in addition to  $\text{CH}_2=\text{NH}$  to account for the products. They also stated that the quantum yield was low, 0.7.

In 1937, Travers<sup>12</sup> and in 1939, Carter<sup>13</sup> and co-workers studied the thermal decomposition with no new results.

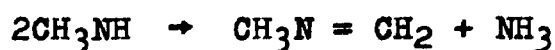
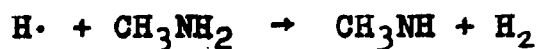
Wetmore and Taylor<sup>14</sup>, in 1944, studied the photolysis at 100°C. finding that the gaseous products were hydrogen, ammonia and traces of methane. They found that the decomposed methylamine to hydrogen ratio was 2:1 at the start of the reaction, but towards the end of the reaction, the ratio was 1:1. The ammonia methylamine ratio was a constant ratio of 0.5 throughout the decomposition. They suggested the following scheme.



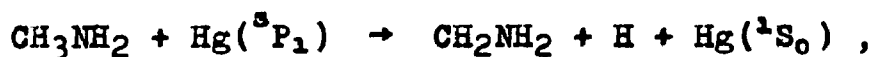
Watson and Darwent<sup>15</sup> in 1952 studied the mercury photosensitized decomposition of methylamine and indicate the primary step as



Additional steps in the mechanism:



With deuterated methylamine,  $\text{CH}_3\text{ND}_2$ , they found that an additional primary hydrogen abstraction step may be operative.



or else the following reaction may occur.

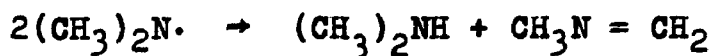


Recently, Meadows and Kirland<sup>16</sup> have attempted to identify the liquid products. Using fast flow pyrolysis, they trapped out and identified a number of products by gas chromatography. Three products isolated from pyrolysis of methylamine were hexahydro 1,3,5-trimethyl-S-triazine ( $\text{C}_6\text{H}_{15}\text{N}_3$ ), N-methylglycinonitrile ( $\text{C}_3\text{H}_6\text{N}_2$ ), and glycinonitrile ( $\text{C}_2\text{H}_4\text{N}_2$ ). A polymer was also observed which contained these functional groups: NH ; C=NH ; C=NR and CN.

## 2. Dimethylamine and Trimethylamine

Romney<sup>17</sup> in 1878 passed trimethylamine through a heated tube and obtained hydrocarbons, hydrogen cyanide, ammonia and a red liquid as products.

Bamford<sup>18</sup> in 1939 studied the photolysis of both dimethylamine and trimethylamine. The products of the dimethylamine photolysis were mainly hydrogen, a brown liquid and small amounts of methane and ethane. He suggested the following mechanism:



This was based upon the fact that when propylene was present, propane and hexane were products, indicating presence of hydrogen atoms.

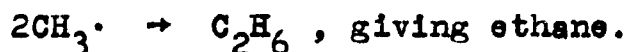
With trimethylamine, similar products were obtained. The primary act here being:



Followed by



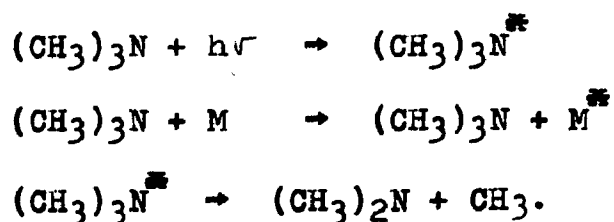
giving methane and



Carter<sup>13</sup> and his co-workers studied the thermal decomposition of the two gases at 440°C. They suggested a free radical mechanism was operative in dimethylamine decomposition and a chain mechanism for trimethylamine. In the latter case, methane formation was retarded by a packed tube, but accelerated by the presence of helium.



In 1957, Gesser<sup>19</sup> and co-workers reinvestigated the photolysis of trimethylamine. If the decomposition was held to less than 1%, the products were methane, hydrogen and ethane. A polymer was formed on greater decomposition. The presence of cyclopentane decreased the rate of hydrogen formation indicating the absence of hydrogen atoms in the reaction. Cyclopentane could also quench the trimethylamine, if it were excited. They proposed the following mechanism:



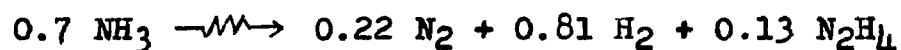
\*excited

M is another molecule or wall.

The pyrolysis of dimethylamine by Meadows and Kirkland<sup>16</sup> gave hexahydro 1,3,5-trimethyl-S-triazine, ( $\text{C}_6\text{H}_{15}\text{N}_3$ ), N,N-dimethylglycinonitrile ( $\text{C}_4\text{H}_8\text{N}_2$ ) and a polymer film as products. Trimethylamine yielded hexahydro 1,3,5-trimethylglycinonitrile ( $\text{C}_6\text{H}_{15}\text{N}_3$ ), N, N-dimethylglycinonitrile ( $\text{C}_4\text{H}_8\text{N}_2$ ) and glycinonitrile ( $\text{C}_2\text{H}_4\text{N}_2$ ). Other products were ethylene and acetonitrile, the latter being detected by mass spectrometer.

#### D. Previous Gamma Irradiation Studies

The radiolysis of liquid ammonia by Cleaver<sup>20</sup> and co-workers showed that nitrogen, hydrogen and hydrazine were produced. The radiolysis can be described by the following equation:



The ratio of hydrogen atoms to nitrogen atoms in the identified products is 3.03. They also found that the  $G(H_2)$  was independent of dose.

The radiolysis of trimethylamine at  $-78^\circ C$ . was carried out by Smith and Swan.<sup>21</sup> The products N,N,N,'N' tetramethylethylenediamine and N,N,N,'N' tetramethylmethylenediamine were explained on the basis of radical combinations.

More recently, Toi, Peterson and Burton<sup>22</sup> studied the effect of density in the radiolysis of ammonia. The density range covered was from  $5.5 \times 10^{-4}$  gm/cc to  $3.12 \times 10^{-1}$  gm/cc at  $137^\circ C$ . The only products detected were hydrogen and nitrogen.

They found the  $G(H_2)$  and  $G(N_2)$  varied with density.  $G(-NH_3)$  were estimated from the values for  $G(H_2)$  assuming that  $G(-NH_3) = \frac{2}{3}G(H_2)$ .  $G(H_2)$  varied from 1.13 to 6.18 molecules per 100 e.v., the latter value at least density. The  $G(-NH_3)$  estimated with  $G(H_2) = 6.18$  is 4.1 molecules per 100 e.v. This value is for ammonia at a density of  $5.5 \times 10^{-4}$  gm/cc.

The only other  $G(-NH_3)$  reported is  $3.27^{23}$  molecules per 100 e.v. at  $20-23^\circ C$ .

## EXPERIMENTAL

### A. Chemicals

#### 1. Ammonia and the Methylamines

Ammonia and the methylamines were purchased from the Matheson Co.

a. Ammonia, anhydrous, purity 99.95% was degassed. A center cut was taken and distilled from a trichloroethylene-dry ice slush bath ( $-80^{\circ}\text{C}.$ ) to a liquid nitrogen bath ( $-195^{\circ}\text{C}.$ ).

b. Methylamine, anhydrous, purity 98%, was first analyzed by gas chromatography. Impurities detected were ammonia, dimethylamine and trimethylamine. Methylamine was degassed and a center cut distilled from  $-80^{\circ}\text{C}.$  to  $-195^{\circ}\text{C}.$  Following this, the gas was subjected to cycles of freezing and thawing, using a slush bath of n-propyl alcohol and liquid nitrogen ( $-130^{\circ}\text{C}.$ ). At  $-130^{\circ}\text{C}.$ , trimethylamine and ammonia have sufficient vapor pressures and can be removed slowly by pumping. Checks on the removal were made at intervals by gas chromatography. Dimethylamine remained as the major impurity.

c. Dimethylamine, anhydrous, purity 99%, was treated in the same manner as methylamine. Methylamine remained as the major impurity.

d. Trimethylamine, anhydrous, purity 99%, was degassed and a center cut distilled from  $-130^{\circ}\text{C}.$  into a bulb at  $-195^{\circ}\text{C}.$  Gas chromatography showed ammonia as an impurity

along with an unidentified compound.

2. Other Chemicals and Gases

- a. Hydrogen, Matheson, prepurified, purity 99.9%
- b. Methane, Matheson, C.P. grade, purity 99.0%
- c. Ethane, Phillips Petroleum Co., purity 99.96%
- d. Ethylamine, Matheson, anhydrous, purity 98.5%
- e. Argon, Matheson, purity 99.998%
- f. Helium, Matheson, purity 99.99%
- g. Methyl hydrazine, K and K Laboratories, Jamaica, N. Y.
- h. Dimethylethylamine, K and K Laboratories, Jamaica, N. Y.
- i. Nitric Oxide, Matheson, purity 99%
- j. Iodine, Matheson, Coleman and Bell, U.S.P.

3. Chromatographic Column Materials

- a. Silica gel, Matheson, Coleman and Bell, 30-60 mesh.
- b. Molecular sieve 13X, Burrell Corp., less than 40 mesh.
- c. Fluoropak 80, Fluorocarbon Co., full range particle size.
- d. Firebrick C-22, Johns-Manville Co., 40-80 mesh.
- e. O-toluidine, Eastman Kodak Co., practical grade.
- f. Diethanolamine, Eastman Kodak Co., practical grade.
- g. Lauryl alcohol, Matheson, Coleman and Bell, technical grade.

- h. Sodium iodide, Mallinckrodt Co., reagent grade
- i. Cetyl alcohol, Fischer Chemical Co., N.F. grade

## B. Equipment and Apparatus

### 1. Cobalt 60 Source

The construction and operation of this source has been previously described<sup>1</sup>. The source had a strength of 85 curies in September 1962. The average dose rate calibrated with a Fricke dosimeter solution at this time was  $8.94 \times 10^{16}$  e.v.  $\text{gm}^{-1}\text{min}^{-1}$ . An impression of the source, to determine its position in the irradiation can, showed that it was not centered. The various irradiation positions used had to be calibrated.

### 2. Gas Chromatograph

A Perkin-Elmer model 154B gas chromatograph was used. In order to minimize temperature variation due to temperature changes in the room, the column chamber was insulated.

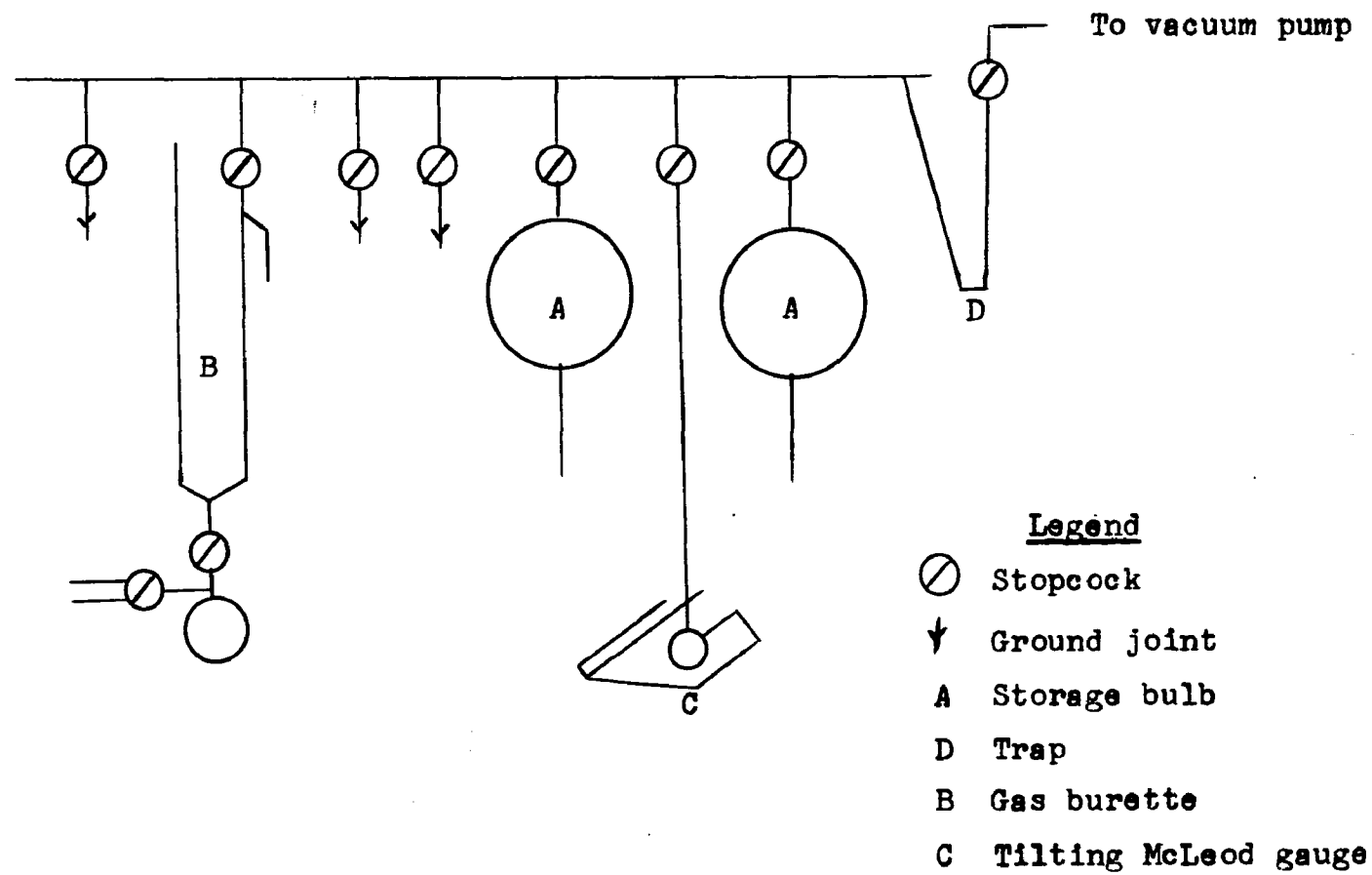
The signal output was recorded on a Sargent SR recorder, utilizing various millivolt spans and chart speeds.

### 3. Vacuum System

The vacuum system used throughout the work is diagrammed in Figure 1. The main manifold consisted of a tilting McLeod gauge (1 micron) attached through a stopcock, a calibrated gas burette, taped storage bulbs to cut out photochemical decomposition and several 10/30 standard tapered joints connected through stopcocks to which the irradiation tubes were attached and other accessories.

Vacuum was obtained with a mercury diffusion pump,

FIGURE I - Vacuum System



and a Cenco Hyvac forepump. The forepump was protected by a water condenser and a dry ice trap. The main manifold was protected from mercury vapors by a liquid nitrogen trap placed between it and the diffusion pump. The volume of the main manifold was calibrated.

#### 4. Toepler Pump

The toepler pump used to transfer non-condensable gases from the irradiated gases is pictured in Figure IIa. The pump was portable and connected to the vacuum manifold through a standard tapered joint. A piece of heavy walled tygon tubing was used to connect the three-way Y stopcock to the tapered joint.

A calibrated volume, 0.31 milliliters between stopcocks A and B, was used to measure the quantity of non-condensable gas. The pressure of the gases in this calibrated volume was measured with a meter stick.

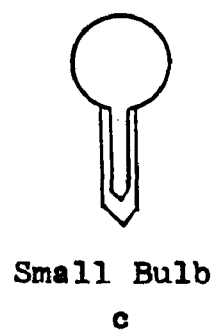
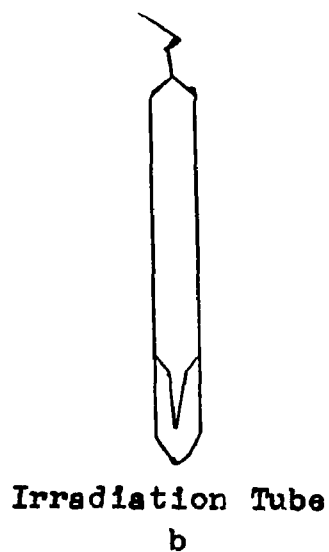
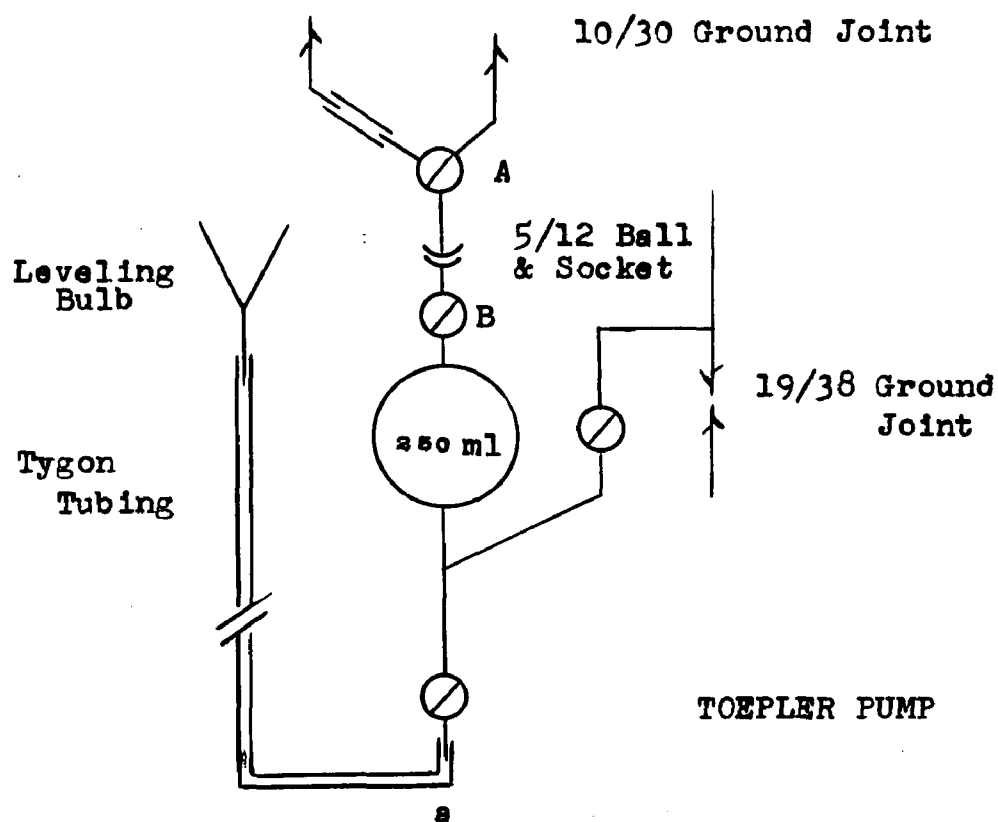
#### 5. Irradiation Tubes

The irradiation tubes consisted of 10 mm. O.D. pyrex tubing with one end of the tube drawn out to a capillary and then fashioned into a break seal. Attached to the other end of the tube was a 2 mm. capillary with a 10/30 standard tapered joint. The individual tubes were checked thoroughly before use for leaks.

The total length of the tubes varied between 4.5 and 5.0 inches. The approximate volume of the tubes was determined after the contents were analyzed. A tube is diagramed in Figure IIb.

FIGURE II

Toepler Pump      Irradiation Tube





## 6. Gas Sample Holders for Gas Chromatographic Analysis

Figure III illustrates the holders into which the gas were transferred for analysis. The gas sample holder in Figure IIIa was used for all analyses, except for the qualitative nitrogen determination.

For the nitrogen determination the holder in Figure IIIb was used. Into this holder a small bulb (see Figure IIc), blown from 2 mm pyrex capillary tubing and into which a sample for analysis had been transferred, was placed. After the holder was flushed with helium, the bulb was broken by tapping the glass rod, releasing the sample into the helium stream.

### C. Procedures

#### 1. Calibration of Source by Fricke Dosimeter<sup>24</sup>

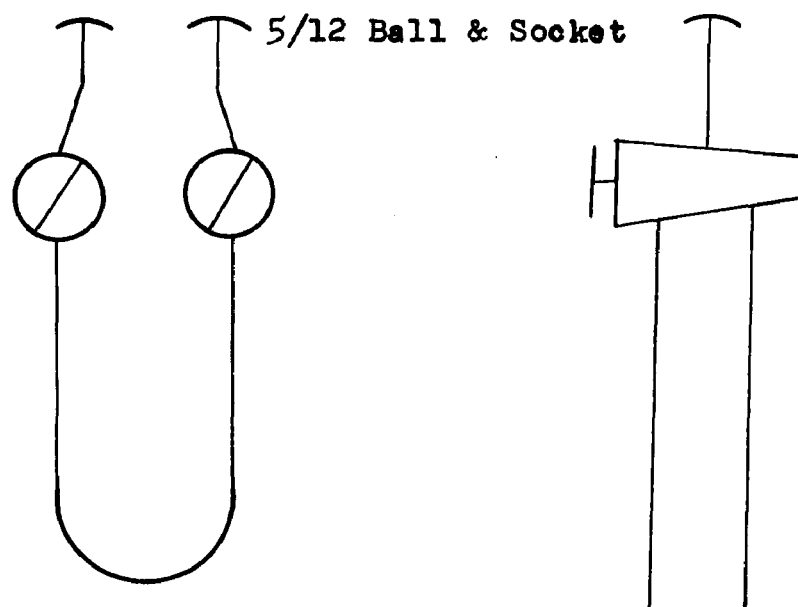
The Fricke solution consists of the following:

$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	$1.98 \times 10^{-3}\text{M}$
$\text{NaCl}$	$1.18 \times 10^{-3}\text{M}$
$\text{H}_2\text{SO}_4$ (95-98%)	$4.0 \times 10^{-1}\text{M}$

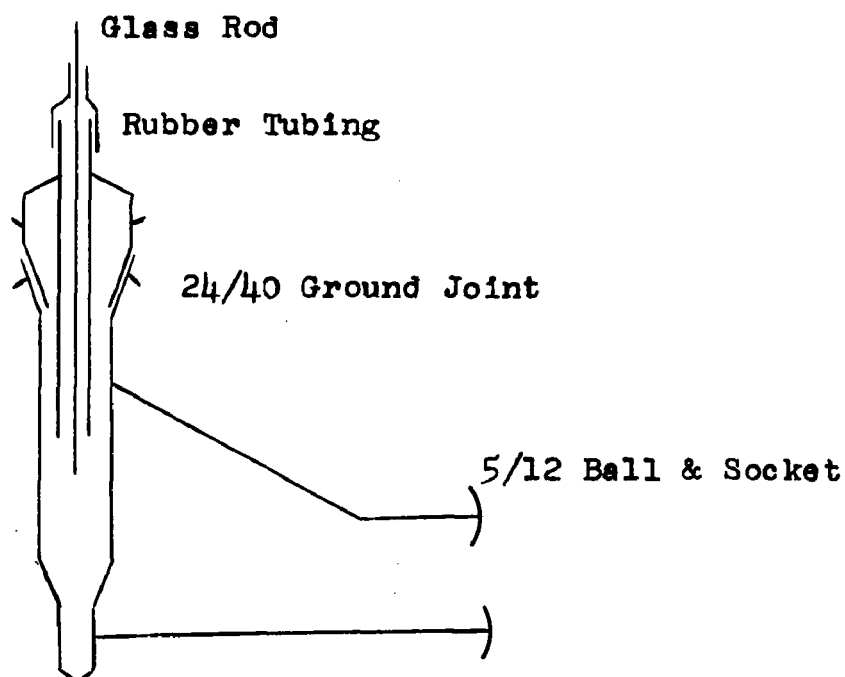
Irradiation tubes were filled to a depth of 4.5 inches with this solution. Eight positions around the wall of the irradiation can were calibrated. Orientation of the can in the source was the same for all irradiations. The dosimeter solutions were irradiated for 6, 10, 15 and 20 minutes. The resulting irradiated solutions were measured on a Beckman DU Spectrophotometer.

Measurement of the absorbance increase in a 1-cm.

FIGURE III  
Gas Sample Holders



a



b

quartz cell at  $3050 \text{ \AA}$  and a slit width of 0.1 mm. was used to determine the yield of  $\text{Fe}^{+2}$  ions produced by irradiation of the Fricke solution. The value of the molar extinction coefficient which was used for  $\text{Fe}^{+2}$  ions at  $3050 \text{ \AA}$  and a temperature of  $23^\circ\text{C}$ . was  $2170 \text{ liter mole}^{-1} \text{ cm}^{-1}$ . The results of the dose rate at various positions in the irradiation can are given in Table 1.

Table 1

## Dose Rate at Various Irradiation Positions

Position No.	Dose Rate - e.v. $\text{gm}^{-1}\text{min}^{-1}$
1	$8.10 \times 10^{16}$
2	$8.33 \times 10^{16}$
3	$9.91 \times 10^{16}$
4	$9.54 \times 10^{16}$
5	$10.8 \times 10^{16}$
6	$7.72 \times 10^{16}$
7	$9.02 \times 10^{16}$
8	$8.24 \times 10^{16}$

## 2. Total Energy Absorbed by Gaseous System

The calculated dose rate from the Fricke dosimeter was used to calculate the energy absorbed by ammonia and the methylamines. Differences must be recognized between the gaseous and liquid systems. The energy absorbed by the Fricke dosimeter is almost entirely due to dissipation from the Compton interactions within the solution itself. In the gaseous

system the energy absorbed results from electrons recoiling into the gas from the container walls. Compton interactions within the gas become important as the gas density increases.

Burton and co-workers<sup>22</sup> applied a correction factor to their work. This was the ratio of  $G(H_2)$  obtained from tritium beta irradiation of ammonia to the  $G(H_2)$  calculated from a Fricke dosimeter. However, the correction factor cannot be applied to the present work since Burton and his co-workers' experiments were done in a steel autoclave.

The energy absorbed by a medium is related to the stopping power of that medium. The stopping power of the medium is proportional to its electron density. The energy absorbed by the gases was calculated as follows:

$$\text{Energy Absorbed(Total Dose) in e.v.} = \text{Dose Rate from Fricke dosimeter e.v. gm}^{-1} \text{ min}^{-1} \times \text{time in minutes} \times \text{gms of sample} \times \frac{\text{electron density of gas}}{\text{electron density of H}_2\text{O}}.$$

To use this ratio of the electron densities, the dosimeter solution and the gas sample must have the same, or nearly the same, stopping power. It is realized that unless this is so, the total dose values calculated are in error. However, this can be corrected once a correction factor as used by Burton can be determined. The electron density ratios used are listed in Table 2.

Table 2

## Electron Density of the Amines and the Electron Density Ratio

Gas	Electron density electrons gm <sup>-1</sup>	Electron Density Ratio
NH <sub>3</sub>	3.54 x 10 <sup>25</sup>	1.06
CH <sub>3</sub> NH <sub>2</sub>	3.48 x 10 <sup>25</sup>	1.04
(CH <sub>3</sub> ) <sub>2</sub> NH	3.48 x 10 <sup>25</sup>	1.04
(CH <sub>3</sub> ) <sub>3</sub> N	3.47 x 10 <sup>25</sup>	1.04

## 3. Calculation of G-value

G value is a means of expressing the yield or consumption of a given specie per 100 e.v. energy absorbed by the system. For example, the formation of hydrogen, expressed as G(H<sub>2</sub>), produced from the radiolysis of ammonia is

$$G(H_2) = \frac{M_{H_2} \times 6.02 \times 10^{23}}{E_{NH_3} \times t \times M_{NH_3} \times MW_{NH_3}}$$

$M_{H_2}$  = moles of hydrogen produced

$E_{NH_3}$  = dose rate in 100 e.v. per gm of ammonia per minute

$t$  = time of irradiation in minutes

$M_{NH_3}$  = total moles of ammonia in the irradiation tube

$MW_{NH_3}$  = molecular weight of ammonia

#### 4. Preparation of Columns

##### a. Pretreatment of firebrick C-22

Firebrick C-22, 40-60 or 60-80 mesh size, was obtained by grinding bricks down in a ball mill and sieving to proper mesh size. The firebrick was then washed to remove dust and dried. The procedure used by James<sup>25</sup> was then followed except for the treatment with base. The firebrick was treated with a 10% methanolic solution of sodium hydroxide. The methanol was decanted off the firebrick and the excess allowed to evaporate off, leaving a crust of sodium hydroxide. The crust was removed and the firebrick dried at 100°C. A study of tailing and peak height (sensitivity) showed that better column properties were obtained with the higher concentration of base.

##### b. O-toluidine Column<sup>1</sup>

The required amount of o-toluidine was added to the pretreated firebrick and the mixture was hand mixed by folding, cutting and stirring to even consistency.

##### c. Cetyl alcohol Column<sup>26</sup>

The required amount of cetyl alcohol was added to the pretreated firebrick, contained in a beaker which was suspended in a 70°C. water bath. The mixture was thoroughly hand mixed and then allowed to cool.

##### d. Diethanolamine-lauryl alcohol-sodium iodide Column<sup>27</sup>

Diethanolamine, lauryl alcohol and sodium iodide were mixed together in the following proportions by weight:

Diethanol amine	72%
Lauryl alcohol	18%
Sodium iodide	10%

Slight heating of the mixture facilitated dissolving the sodium iodide. On cooling, two phases resulted. Before use, this mixture was well shaken. The proper amount was added to Fluoropak 80, used as a support instead of firebrick.

e. Molecular Sieve 13X Column

Before use, molecular sieve 13X was heated at 300°C. for 15 hours and cooled in a dessicator before packing into the column.

f. Silica Gel

Silica gel was used as received. A 10-cm. length of drierite was placed before the silica gel in the column.

All columns were packed in 6 mm O.D. pyrex glass tubing. All columns were conditioned in the gas chromatograph at least 16 hours at operating conditions prior to use. Table 3 lists the column conditions and use. Helium was the carrier gas used throughout work.

5. Procedure for Preparation of Samples

a. Ammonia and Methylamines

The irradiation tube was attached through the 10/30 standard tapered joint to the vacuum manifold, the vacuum line evacuated and the line flamed gently. The stopcock to the pumps was closed, the McLeod gauge read and then its stopcock closed. The storage bulb was opened and the gas allowed to expand to a desired pressure. All stopcocks were

Table 3

## Chromatographic Columns, Conditions and Use

Column	Temp. ±1°C.	Length feet	Flow Rate He ml/min	Separation
1. Silica Gel	26	5.3	45	hydrogen, methane, ethane
2. Molecular Sieve 13X	25	6.7	50	hydrogen, oxygen, nitrogen, methane
3. O-toluidine, 30% by weight supported on firebrick (slow elution of substrate)	22	6.25	32	ammonia, methylamine, dimethylamine, ethyl- amine
4. Cetyl alcohol, 23.6% by weight supported on firebrick	56	11.4	32	ammonia, methylamine, trimethylamine, di- methylamine, ethyl- amine, methyl hydra- zine, dimethylethyl- amine



Table 3 cont.

Column	Temp. ±1°C.	Length feet	Flow Rate He ml/min	Separation
5. Diethanolamine, lauryl alcohol, sodium iodide 5%, by weight supported on Fluoropak 80	35	11.7	38	trimethylamine, ammonia dimethylamine, methyl- amine

closed except the one to the gas burette. The moles of gas were determined from measured pressure, known volume and temperature. The gas was then transferred to the irradiation tube by freezing it into the tube with liquid nitrogen. The McLeod gauge was checked to see that the manifold pressure returned to its original reading before the stopcock to the irradiation tube was closed. The capillary was sealed and the tube removed. Quantitative transfer, better than 99%, was achieved this way.

## 6. Gases plus Scavengers

### a. Helium

The ammonia or methylamines were transferred to the irradiation tube and held at liquid nitrogen temperature and the stopcock to the tube closed.

A helium tank was connected to the manifold through heavy, walled rubber tubing. The serrated outlet nozzle on the tank was replaced with a large diameter smooth nozzle which provided a tighter seal. The connection was evacuated and the entire system flushed with helium several times. A single tube mercury manometer, attached to the vacuum manifold, served as a safety outlet. After the stopcock to the pumps was closed, the manifold was filled to a certain pressure, and the gas burette opened. From the approximate volume of the tube, the final ammonia or amine pressure could be estimated. The amount of scavenger used was between 1 and 2 mole percent. Helium was removed until this amount was indicated by pressure. The vacuum pumps were closed and the

stopcock to the irradiation tube opened. The system was allowed to come to thermal equilibrium, the pressure of helium noted, the stopcock to the irradiation tube closed and the tube sealed and removed.

b. Argon

Argon was introduced into a small storage bulb in a similar manner as helium. Measurements were made in the same way as with helium except that the argon was expanded from the bulb at liquid nitrogen temperature.

c. Iodine

Iodine was resublimed from a mixture with potassium iodide. After degassing the iodine was introduced into the irradiation tube. The iodine tube was immersed into a bath at 20°C. At this temperature iodine has a vapor pressure of 0.2 mm. After introduction of the iodine into the irradiation tube the stopcock was closed and the iodine was kept at liquid nitrogen temperature while the amine was measured. The amine was then frozen into the irradiation tube.

d. Nitric Oxide

Nitric oxide was distilled into the gas burette from an iso-pentane liquid nitrogen slush bath (-160°C.). After attaining thermal equilibrium, the nitric oxide was measured and then transferred into the irradiation tube. The amine followed and then the tube was sealed.

7. Analysis of Irradiated Samples for Hydrocarbons

The irradiation samples were placed in the toepler pump through the 19/38 standard tapered joint, and the toepler

pump evacuated. After evacuation, the stopcock between the sample and the 250-ml. bulb of the toepler pump was closed. A nail enclosed in glass was dropped to break the break seal on the tube. The ammonia or amine was frozen out at  $-160^{\circ}\text{C}$ . After the gas was frozen out, the stopcock to the 250-ml. bulb opened. The non-condensable gases were allowed to expand into this chamber. The stopcock was closed and the non-condensable gases toeplered into the calibrated volume. In the meantime the ammonia or amine was thawed out, then refrozen, the mercury lowered and the same procedure followed again. Three toeplerizations were usually sufficient to give a constant pressure in the calibrated volume. The non-condensable gases were then transferred to the gas sample holder, previously attached through the 10/30 standard tapered joint and an adapter to the toepler pump. The determination of the gases was done on the silica gel column.

The ammonia or amine was transferred to another break seal tube, sealed and stored for further analysis.

To check the above procedure, a known amount of ethane was transferred into an irradiation tube and sealed. The ethane was carried through the above procedure and analyzed on the gas chromatograph. The sample was checked against a previously prepared calibration curve for ethane which showed that 96% of the sample was recovered.

#### 8. Analysis for Nitrogen

The samples were treated in a similar manner as described above except the ammonia or amine was frozen out

at  $-195^{\circ}\text{C}$ . A qualitative determination of the presence of nitrogen was accomplished with the amines. The gas sample holder was replaced with a small bulb (see Figure IIc) blown from 2 mm. capillary pyrex glass and attached to the toepler pump through the 10/30 standard tapered joint. After transfer, the capillary was sealed, the bulb was then broken in the helium stream of the gas chromatograph, using the gas sample holder in Figure IIIb. Analysis for nitrogen was done on molecular sieve 13X.

For ammonia radiolysis both hydrogen and nitrogen could be analyzed on the same column.

#### 9. Analysis of Amines in Irradiated Gases

After the non-condensable gases were analyzed, the collected amine sample was placed in a tube by way of a 19/38 standard tapered joint and attached to the vacuum manifold. After evacuation, the stopcock to the tube was closed and the break seal on the sample tube broken. A sample was transferred to the gas burette, measured, then transferred to the gas sample holder with a liquid nitrogen bath. The gas sample holder was closed, the gas allowed to warm and then analyzed by gas chromatography on the diethanolamine column.

#### 10. Calibration of Hydrogen and Methane

The silica gel column was calibrated with known mixtures of hydrogen and helium and methane and helium.

These mixtures were prepared in one liter bulbs equipped with a stopcock. The bulb was filled to a known pressure with methane or hydrogen. Then helium was quickly

introduced until the final pressure in the bulb was one atmosphere. The stopcock was closed and the gases allowed to mix for 24 hours or mixed by use of dry ice, which sets up convection currents in the bulb.

After mixing, a septum cap was placed over the 8 mm. O.D. arm from the bulb stopcock. Samples of known volume of the mixture were injected into the gas chromatograph using a 100 microliter and a 2500 microliter Hamilton gas syringe. Several separate injections of known volume were made. Peak height was used as a measure of the quantity of gas. Peak heights were reproducible to within 5%. Each attenuation used for analysis was calibrated. All calibration curves, peak height versus microliters of gas injected, were linear for both hydrogen and methane. The calibration curves did not pass through the origin. This was not due to the above method, but the limitation of the recording system.

Since the method of calibration differed from the method of introduction of the samples for analysis, a check between the two methods was made with ethane. A mixture of ethane was prepared with air in a similar manner as above. Methane-air and methane-helium mixture gave the same results. A calibration curve was prepared using the injection method. The other method was the calibration of ethane by measurement

\* See research notebook for data and curves, pp. 149-158

of the ethane in the gas burette and quantitative transfer to the gas sample holder. Introduction into the gas chromatograph was in the same manner as the products from the radiolysis.

Both methods gave linear calibration curves,<sup>\*</sup> not passing through the origin but at  $3 \times 10^{-6}$  moles. The slopes varied slightly. The ratio between the slopes was 1.02.

#### 11. Calibration of Ammonia and Amines

Calibration of Ammonia on the diethanolamine column. was done with mixtures of ammonia and methylamine. Since the analysis for ammonia as a radiolysis product was done with the large percentage of the sample being methylamine, calibration had to be done with such a mixture. Use of ammonia alone was erroneous.

The diethanolamine column along with the o-toluidine and cetyl alcohol suffered from "memory" effects. Previous to calibration or analysis the columns were flushed with the proper amine. For example, to analyze for ammonia formed in the radiolysis of methylamine, the column was flushed with methylamine to elute all previous amines on the column. If this was not done, it led to false product assignments.

Mixtures of ammonia and methylamine were made from measured amounts of the two gases frozen together in the gas sample holder using a liquid nitrogen bath. The gases were

<sup>\*</sup> See research notebook for curves, p. 185

allowed to warm to room temperature before they were flushed into the helium stream and analyzed on the gas chromatograph.

Area under the peak was determined with a planimeter.\* The average of five area determinations was taken. Areas were reproducible to within 10 percent. Peak area versus mole fraction of ammonia was plotted. Figure IV shows the calibration curve for ammonia.

Dimethylamine was calibrated from mixtures of dimethylamine and methylamine. Figure V shows calibration curve, peak height versus mole fraction. Dimethylamine was an impurity in the methylamine and therefore the calibration curve does not pass through the origin. The difference in the peak heights was used to calculate the amount of dimethylamine formed in the radiolysis of methylamine.

Mixtures of trimethylamine and dimethylamine were made to calibrate the formation of trimethylamine from the radiolysis of dimethylamine. Peak area versus mole fraction of trimethylamine is shown in Figure VI.

✱

The author wishes to thank the Civil Engineering Department for the loan of the planimeter and his wife for determinations of the areas.



FIGURE IV

Calibration Curve for Ammonia Present in  
Methylamine

Diethanolamine-Lauryl Alcohol-Sodium Iodide

Column  $35^{\circ}\text{C}$

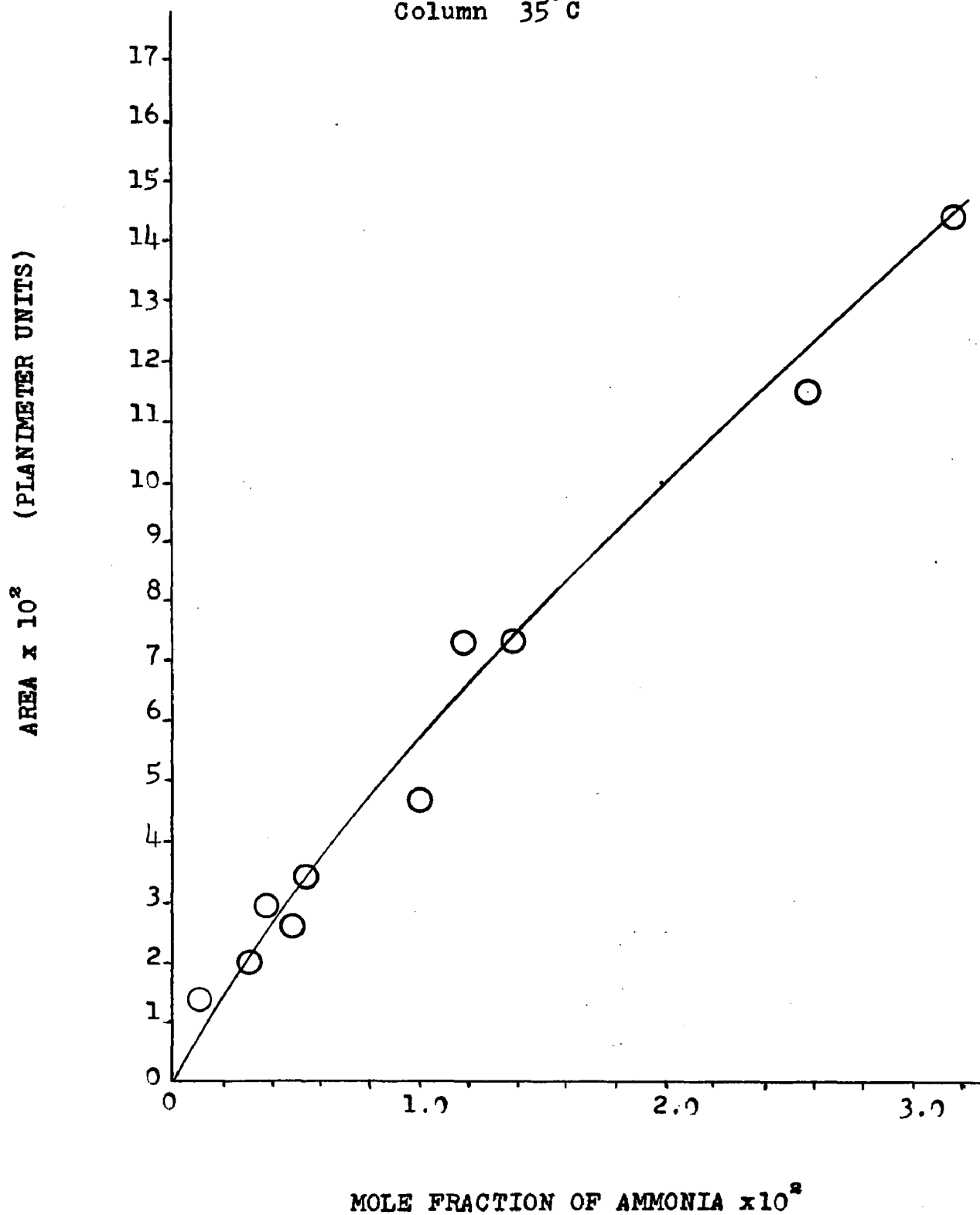


FIGURE V

Calibration Curve for Dimethylamine Present  
in Methylamine

Diethanolamine-Lauryl Alcohol-Sodium Iodide  
Column 35°C

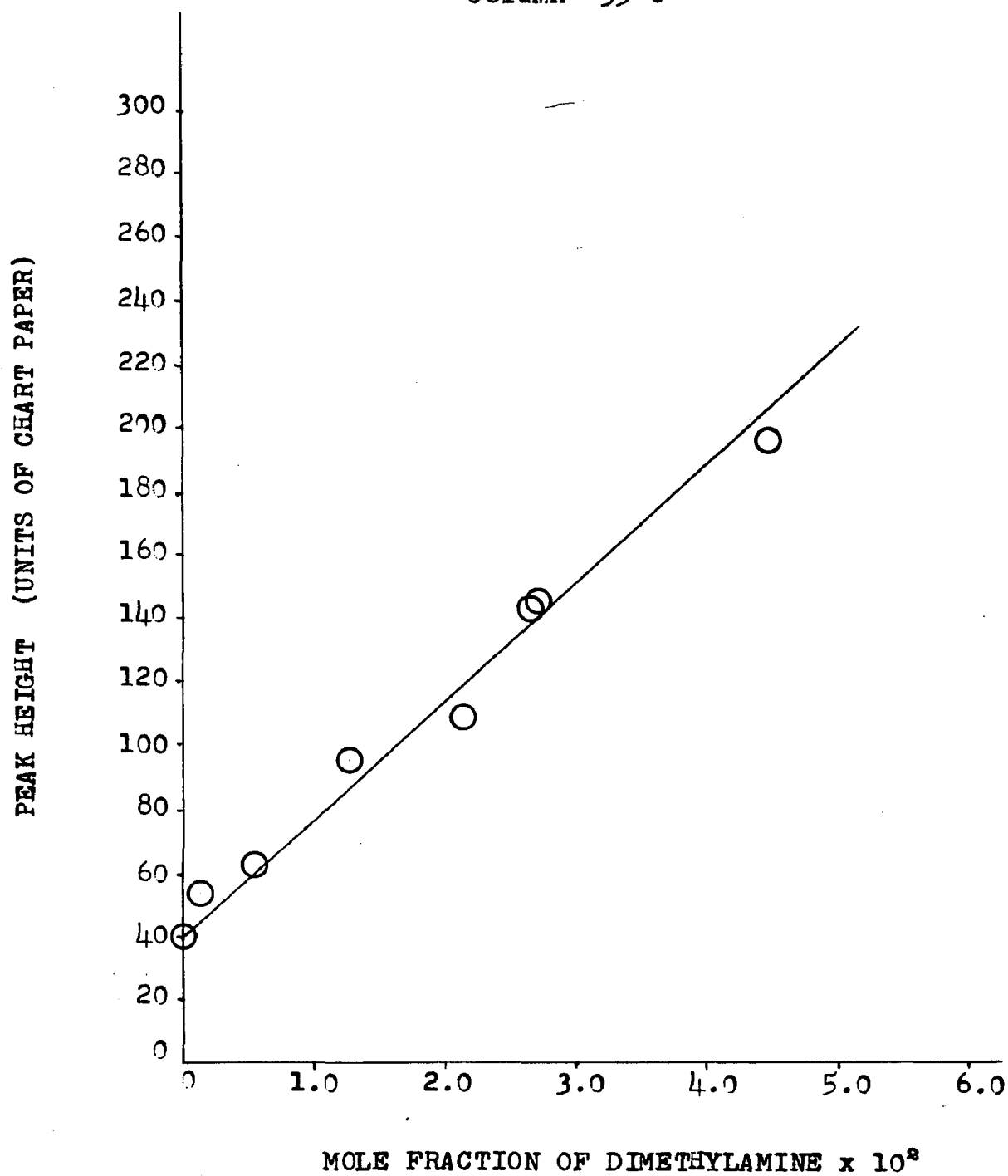
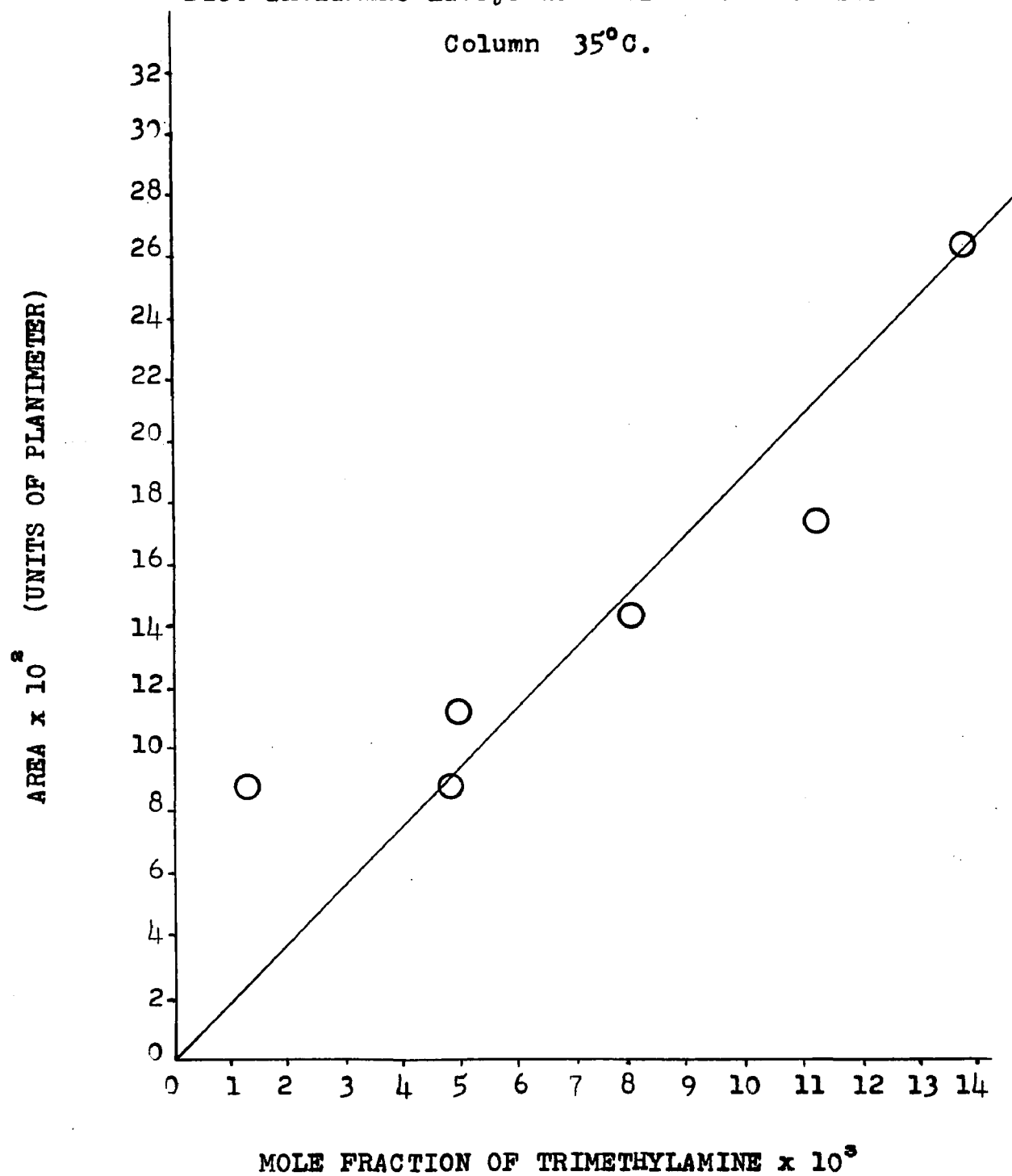


FIGURE VI

Calibration Curve for Trimethylamine Present  
in Dimethylamine

Diethanolamine-Lauryl Alcohol-Sodium Iodide

Column 35°C.



## RESULTS AND DISCUSSION

The primary purpose of this work was to identify the products of the radiolysis of ammonia and the methylamines.

By using gas chromatography as the analytical tool, some products may have escaped detection. The identification of a product was checked against a known and where possible, confirmed on a second column. For example; ammonia was identified as a product from the radiolysis of methylamine on the diethanolamine-lauryl alcohol-sodium iodide column and confirmed on the o-toluidine column.

The quantitative determinations for hydrogen and methane are within 10 per cent. The error in the determinations of ammonia and dimethylamine may be higher because of difficulties with the columns.

An end product may be formed by many paths. Some are more important than others. It is difficult to distinguish different rates with the present information. However, mechanisms have been postulated to show possible paths to end products.

The occurrence of ion-molecule reactions in the mass spectrometer and the accounting of product yields, using these data, has met with much success. Futrell<sup>28</sup>, in an investigation of the radiolysis of n-hexane and n-pentane, has shown that the yields and nature of the observed products can be predicted with accuracy. Mass spectrometric data on the

methyamines has been included for possible future use.

#### A. Gamma Radiolysis of Ammonia

Nitrogen and hydrogen were the only products detected following the radiolysis of ammonia. Hydrazine was a suspected product, but previous radiolytic and photolytic studies have shown that it is not produced in a static system, and it was not found in this work.

The hydrogen yield determined, using the silica gel column, is plotted in Figure VII. Hydrogen production increases with irradiation time. The initial G value,  $G_{H_2}^0$ , determined from the initial slope of the plotted curve, was 10.

Table 4 presents the  $G_{H_2}$  value for each irradiated sample. Reproducibility of the data is indicated by samples 65 and 66, 68 and 69. The results agree within 10%. The differences can be attributed to variation in the dose received by the samples due to their relative position in the irradiation.

The G value is in good agreement with that reported by Toi, Peterson and Burton.<sup>22</sup> A value of 9.8 for  $G_{H_2}$  was obtained at a similar density. This value was determined by use of the Fricke dosimeter for calibration and is the uncorrected value. As previously stated in the experimental section, the absolute G values may be in error, since a liquid dosimeter was used and the results applied to a gaseous system.

The irradiations of Toi, Peterson and Burton were done at 137°C. The experiments reported here were done at ambient

TABLE 4

## Radiolysis of Ammonia

<u>Sample No.</u>	<u>Position in Source</u>	<u>Irradiation Time (minutes)</u>	<u>Total Dose ev x 10<sup>-18</sup></u>	<u>Initial Moles of NH<sub>3</sub> x 10<sup>+4</sup></u>	<u>Mole % Added Inert</u>	<u>Molecules of H<sub>2</sub> Formed x 10<sup>-16</sup></u>	<u>G Value</u>
24	4	5145	1.82	2.05	—	11.5	6.33
63	1	13625	5.11	2.57	—	43.4	8.50
65	8	5809	2.22	2.57	—	21.7	9.78
66	7	5809	2.28	2.42	—	22.9	10.0
68	2	16136	7.32	2.64	—	57.2	7.82
69	3	16136	7.61	2.64	—	55.4	7.28
71	6	12963	4.72	2.62	—	41.6	8.82
43SHe	5	10841	5.04	2.38	1.65	28.3	5.62
50SAr	1	17038	6.55	2.56	1.56	60.2	9.19
51SAr	2	11480	4.78	2.69	1.63	31.9	6.68

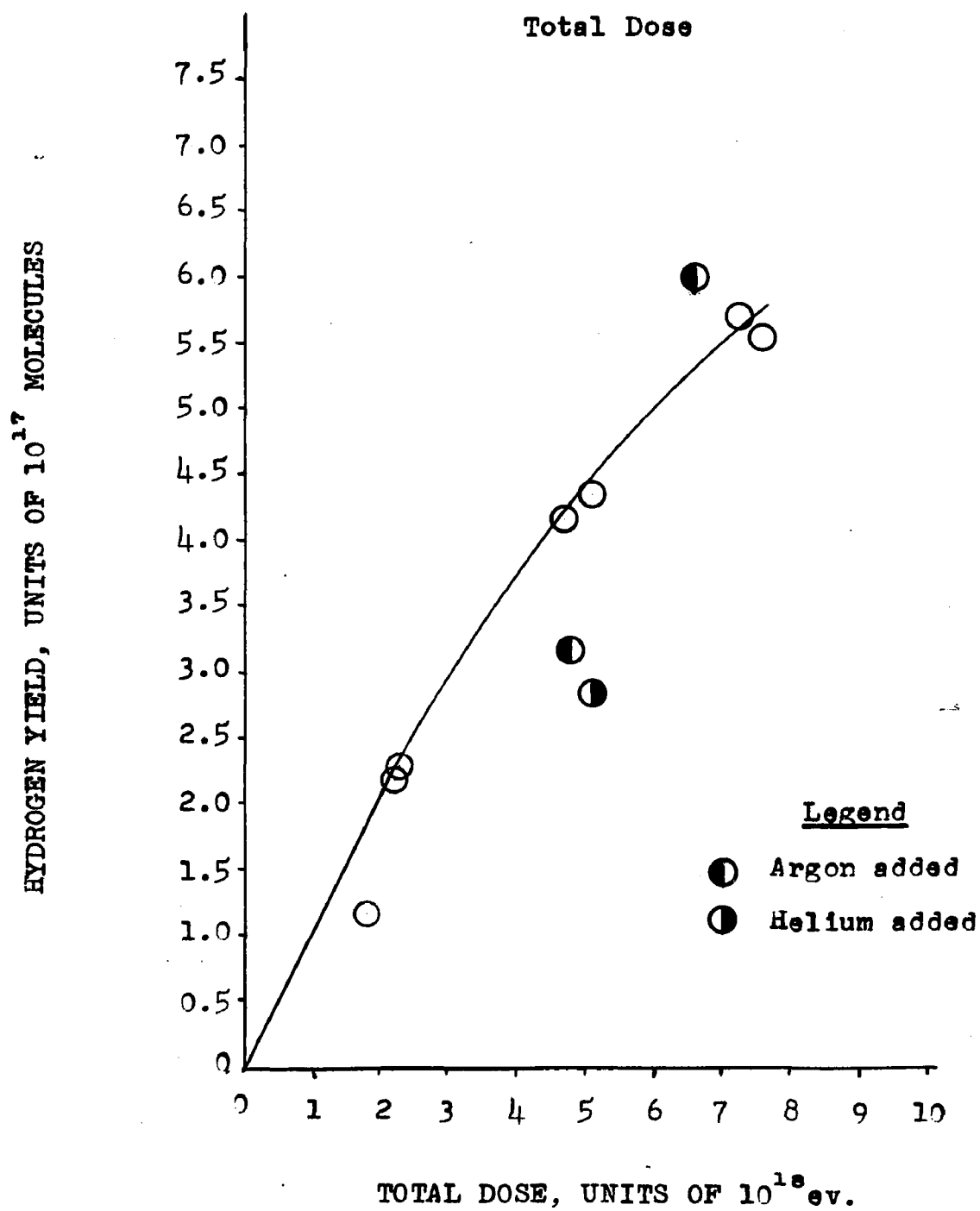
FIGURE VII

 $\gamma$ -Radiolysis of Ammonia

Yield of Hydrogen

vs

Total Dose



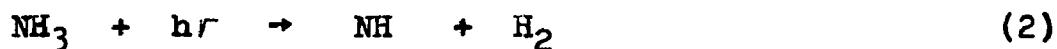
temperature.

The  $G(-NH_3)^0$  can be calculated from  $G_{H_2}^0$  using the stoichiometric decomposition of ammonia. This yields a value of 6.6.

The determination of hydrogen and nitrogen was attempted simultaneously by using the molecular sieve column. However, the indication of oxygen, due to traces of air in the stopcocks of the gas sampler, meant erroneous results for nitrogen. An approximation, of the nitrogen formed, was obtained using air for the calibration and the oxygen, nitrogen peak ratios. The hydrogen to nitrogen yield should be 3 to 1. The nitrogen yield was  $0.23 \times 10^{17}$  molecules for a total dose of approximately  $7 \times 10^{18}$  ev. On the basis of the above ratio, the nitrogen yield should have been  $1.6 \times 10^{17}$  molecules. The value obtained is low and this may well be due to the poor resolution of the nitrogen by the above method.

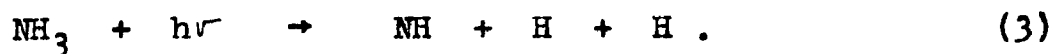
The mechanism for the production of hydrogen and nitrogen is not well understood even though extensive investigations have been made.

The ultraviolet absorption spectrum of ammonia gas extends from  $2400 \text{ \AA}$  to  $1665 \text{ \AA}$  in diffuse bands.<sup>29</sup> Excitation of ammonia in this region leads to predissociation by two paths.





Below 1550 Å another process<sup>30</sup> may occur

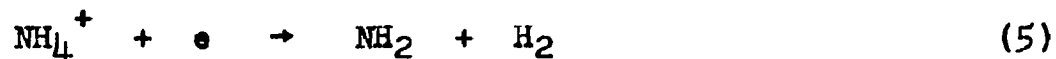


Work with  $\text{C}_2\text{D}_4$ <sup>31</sup>, a scavenger for hydrogen atoms, showed that at 1236 Å, 14% of the decomposition proceeds by reaction (2), molecular elimination of hydrogen.

Excitation is not the only means by which chemical intermediates are formed. Ionization processes can also lead to intermediates which eventually go to products. Mass spectrometric studies show that ions such as  $\text{N}^+$ ,  $\text{NH}^+$ ,  $\text{NH}_2^+$  and  $\text{NH}_3^+$  are produced from electron impact of ammonia. At higher pressures,  $\text{NH}_4^+$  has been observed resulting from the following reaction:



Neutralization of these ions by electron capture can occur.  $\text{NH}_4^+$  neutralization is considered to be an important reaction due to its high rate of formation.<sup>5</sup>



Reaction (6) is favored over (5).

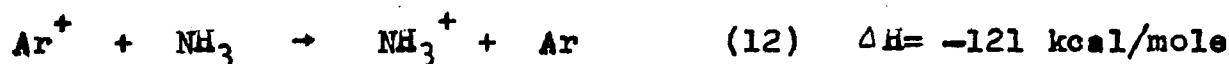
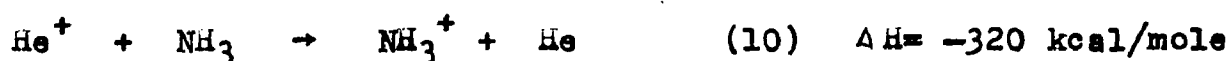
The absence of hydrazine in the static system is due to its destruction by hydrogen atoms via reactions (7) and (8).



Evidence for charge transfer was found by adding the inert gases, helium and argon, to some of the samples. The

energy transferred should follow the same trend as the ionization potentials. The ionization potentials<sup>6</sup> are helium (24.58 v), argon (15.76 v) and ammonia (10.15 v). The results (see Table 4 and Figure VII) indicate a decrease in the hydrogen yield with helium and a decrease with one sample and an increase with the other, when argon is added. It is difficult to explain this effect. Impurities present may account for the observed inhibition results.

Ionization of helium and argon can occur. These ions can then react with ammonia via the following reactions:



The heat of reaction values were calculated from the heats of formation of the various species.<sup>32</sup> Since the heats of formation may vary a few kilocalories per mole, reaction (11) may well be endothermic. The reactions would all result in an increase of the hydrogen yield. The formation of hydrogen atoms by reactions (9) and (11) would also reduce the hydrazine formation.

As the concentration of hydrogen increases, reaction of hydrogen with ionized inert gas becomes more probable.



Reaction (13) has been observed in the mass spectrometer.<sup>33</sup>

The formation of nitrogen is given by the following reactions with hydrazine and  $\text{NH}_2$  radicals.<sup>34</sup>



The direct proof for or against these reactions is non-existent at present. Reactions (15) and (16) were postulated for nitrogen formation from results obtained in solution.

#### B. Gamma Radiolysis of Methylamine

Radiolysis of methylamine resulted in methane, hydrogen, ammonia and dimethylamine as products. These were the only products detected by gas chromatography. There was no indication of the formation of nitrogen. Ethylamine, a suspected product, was undetected, but could very well be present. Ethylamine elutes after the methylamine on the o-toluidine column and a small concentration may be masked by the tailing of the methylamine peak. Ethane was also undetected. The lowest detectable limit on ethane was  $1 \times 10^{18}$  molecules. Any formation of ethane below this amount would go unnoticed. Polymer or liquid formation was not observed.

The observations of hydrogen, methane and ammonia as products agree with the photochemical studies.

The results for hydrogen, methane, ammonia and dimethylamine formation are plotted in Figures VIII through XI and tabulated in Table 6. The products were observed over a thirty-fold change in total dose.

From the initial slopes, the  $G^0$  values were determined.

TABLE 5

## Radiolysis of Methylamine

<u>Sample No.</u>	<u>Position in Source</u>	<u>Irradiation Time (minutes)</u>	<u>Total Dose ev x 10<sup>-18</sup></u>	<u>Initial Moles of CH<sub>3</sub>NH<sub>2</sub> x 10<sup>-4</sup></u>	<u>Moles of Added Scavenger x 10<sup>-6</sup></u>	<u>Mole % Added Scavenger</u>
9	1	16984	18.5	4.17	—	—
11	3	7226	8.89	3.85	—	—
13	2	28526	30.7	4.01	—	—
58	2	5558	6.24	4.18	—	—
59	3	15725	20.8	4.15	—	—
60	5	11115	16.6	4.29	—	—
78	5	1625	2.41	4.26	—	—
61SI <sub>2</sub>	6	15725	16.3	4.17	0.2 mm I <sub>2</sub>	—
30	2	9943	6.03	2.26	—	—
31	1	20080	11.0	2.11	—	—

TABLE 5 cont.

<u>Sample No.</u>	<u>Position in Source</u>	<u>Irradiation Time (minutes)</u>	<u>Total Dose ev x 10<sup>-18</sup></u>	<u>Initial Moles of CH<sub>3</sub>NH<sub>2</sub> x 10<sup>-4</sup></u>	<u>Moles of Added Scavenger x 10<sup>-8</sup></u>	<u>Mole % Added Scavenger</u>
32	7	15530	10.9	2.42	—	—
33	2	10137	6.56	2.42	—	—
34	8	6637	4.28	2.43	—	—
44SHe	6	10841	6.30	2.33	3.32	1.41
52SAr	3	11480	10.3	2.75	4.24	1.52
53SAr	4	17038	14.5	2.74	4.18	1.50

TABLE 6

## Radiolysis of Methylamine - Products and G Values

Sample No.	Molecules of $H_2$ Formed $\times 10^{-17}$	$G_{H_2}$	Molecules of $CH_4$ Formed $\times 10^{-18}$	$G_{CH_4}$	Molecules of $NH_3$ Formed $\times 10^{-17}$	$G_{NH_3}$	Molecules of $(CH_3)_3NH$ $\times 10^{-17}$
9	21.3	11.5	12.0	0.65	24.5	13.2	62.6
11	N.D.*	N.D.	N.D.	N.D.	36.6	41.2	1.16
13	21.9	7.14	13.5	0.44	23.6	7.69	-10.3 <sup>+</sup>
58	5.60	8.98	3.73	0.598	5.30	8.50	7.53
59	20.2	9.72	8.19	0.394	18.2	8.76	7.53
60	18.4	11.1	7.53	0.454	N.D.	N.D.	N.D.
78	2.47	10.2	N.D.	N.D.	3.64	15.1	11.0
61SI <sub>2</sub>	20.1	12.3	9.70	0.595	11.9	7.31	-6.25 <sup>+</sup>
30	6.20	10.3	3.01	0.497	3.65	6.03	N.D.
31	11.4	10.4	5.39	0.490	4.70	4.27	N.D.

\*N.D. - not determined

<sup>+</sup> negative sign indicates decrease of dimethylamine

TABLE 6 cont.

Sample No.	Molecules of $H_2$ Formed $\times 10^{-17}$	$G_{H_2}$	Molecules of $CH_4$ Formed $\times 10^{-16}$	$G_{CH_4}$	Molecules of $NH_3$ Formed $\times 10^{-17}$	$G_{NH_3}$	Molecules of $(CH_3)_3NH$ $\times 10^{-17}$
32	10.8	9.92	5.00	0.459	5.22	4.79	N.D.
33	8.19	12.5	3.98	0.606	2.76	4.21	N.D.
34	4.70	11.0	2.59	0.605	N.D.	N.D.	N.D.
44She	N.D.	N.D.	N.D.	N.D.	36.3	57.6	-2.81 +
52SAr	11.0	10.7	4.72	0.458	12.8	12.4	5.78
53SAr	15.2	10.5	6.08	0.419	10.1	6.97	3.30

+negative sign indicates decrease of dimethylamine

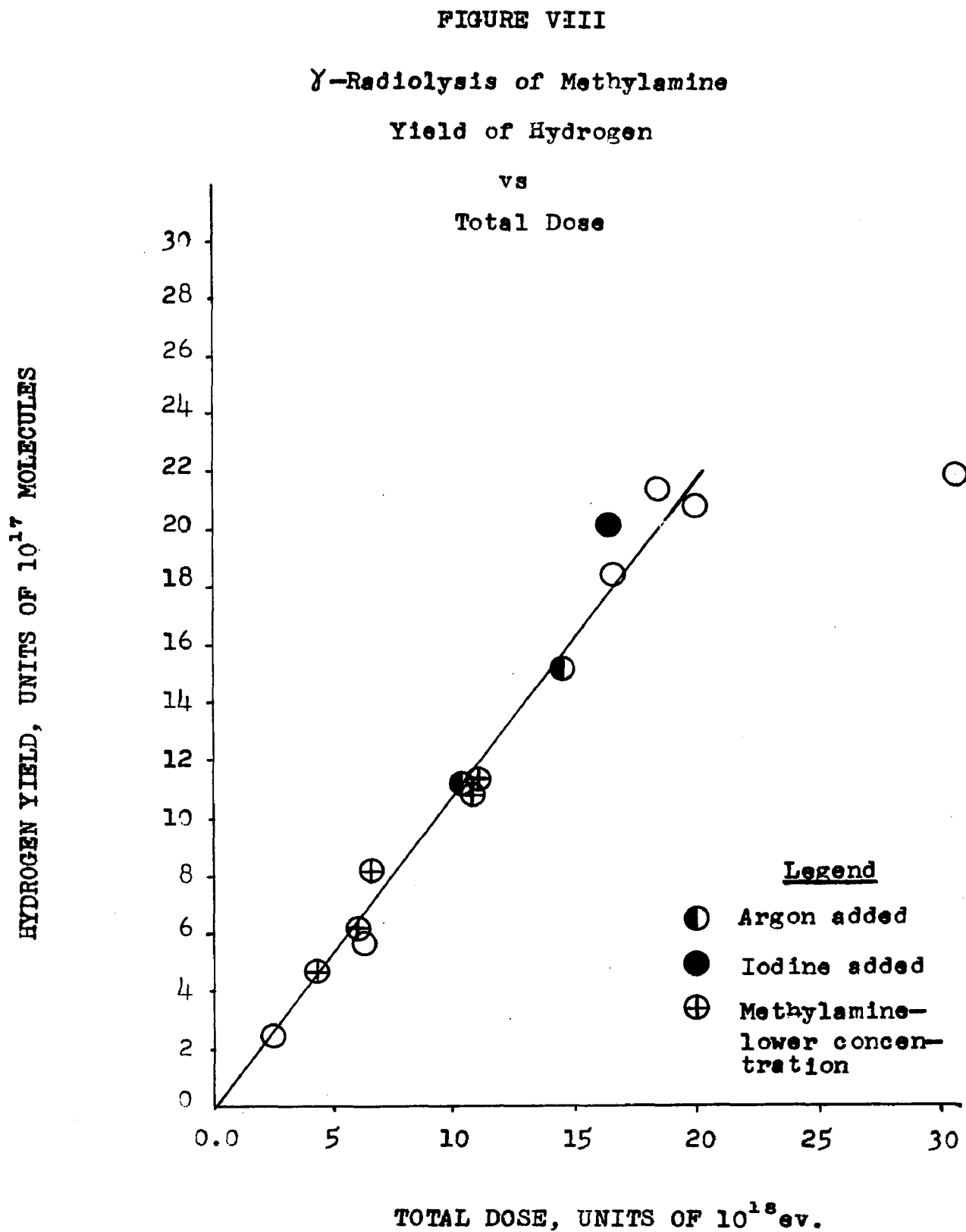




FIGURE IX

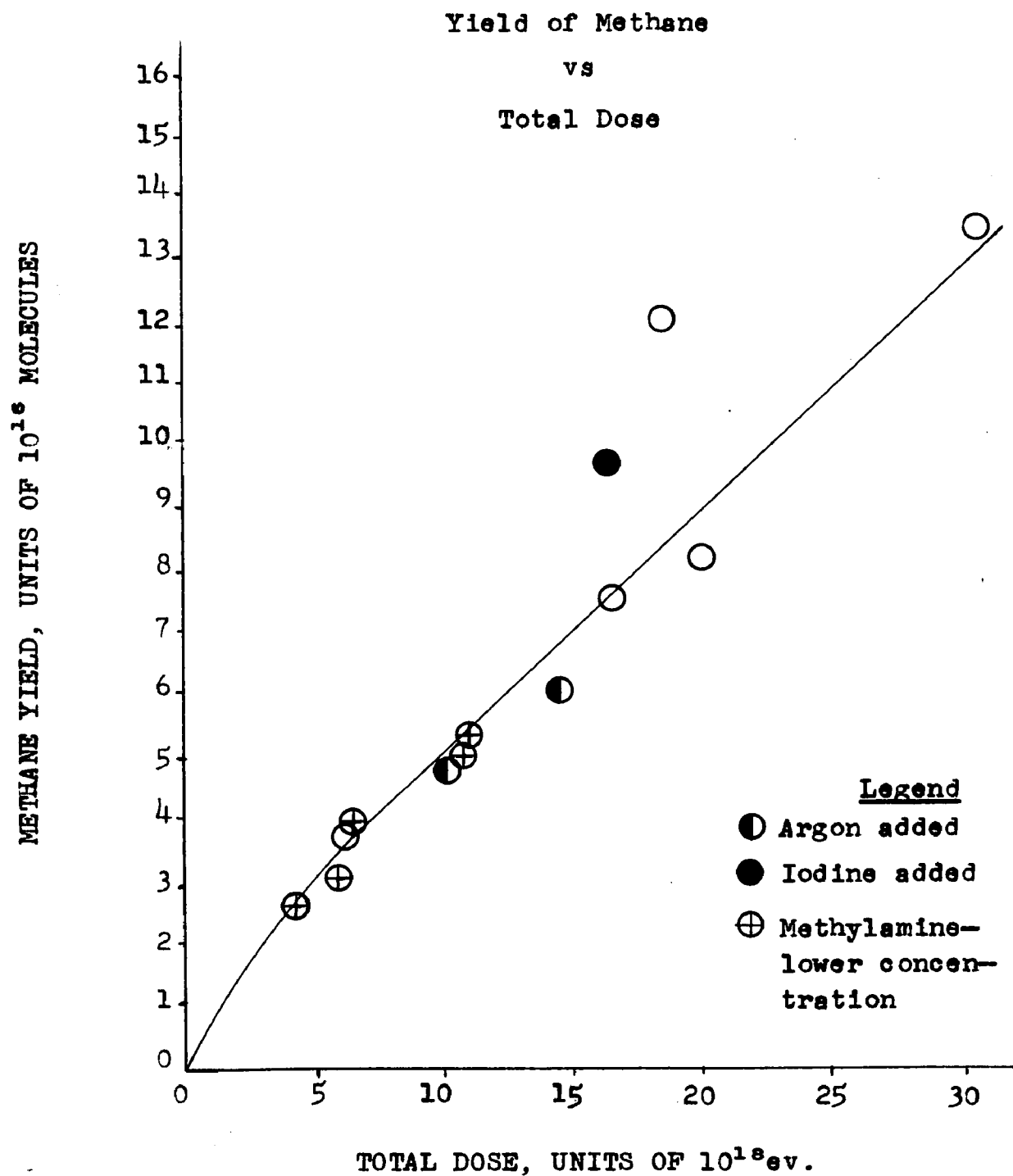
 $\gamma$ -Radiolysis of Methylamine

FIGURE X

 $\gamma$ -Radiolysis of Methylamine

Yield of Ammonia

vs

Total Dose

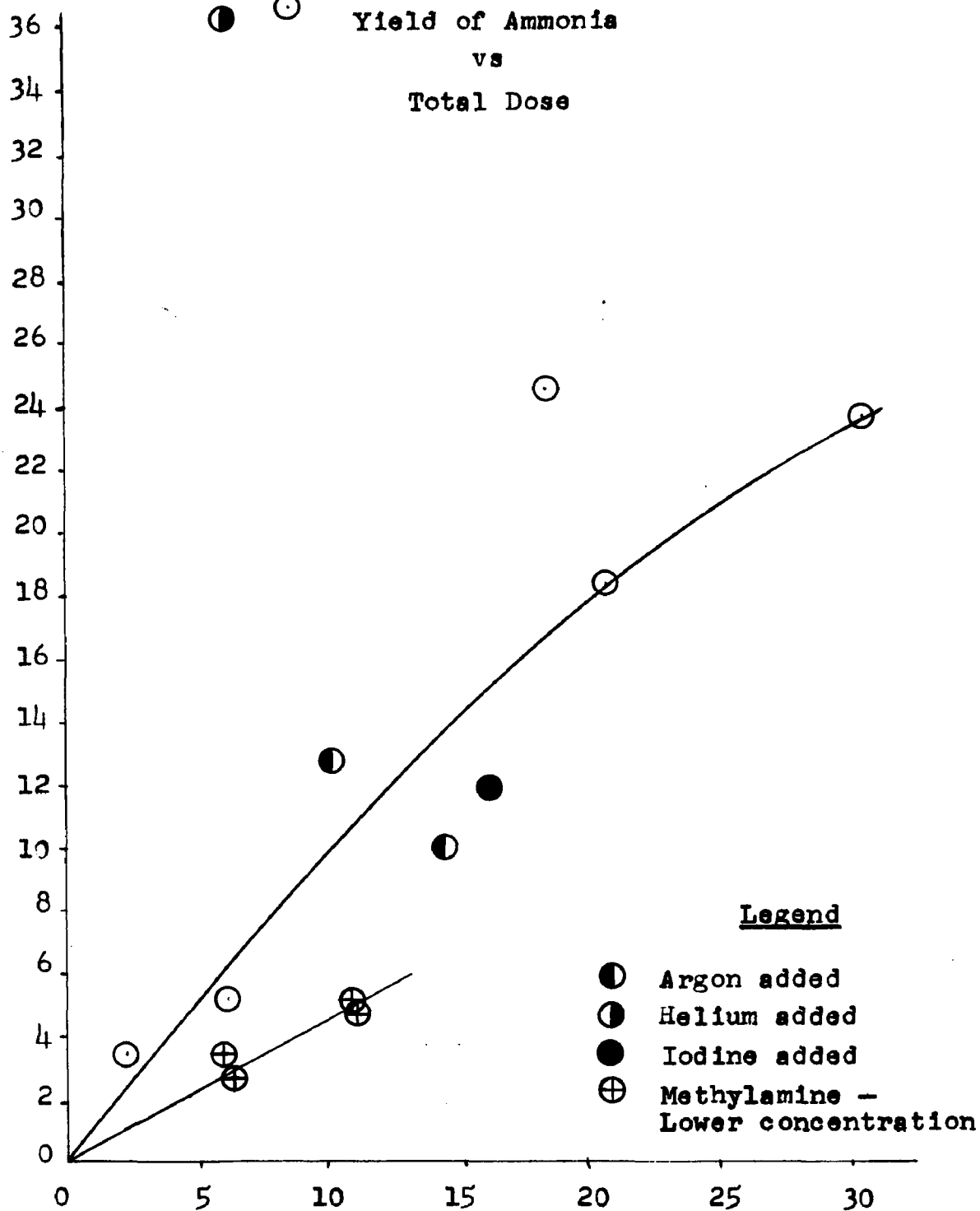
AMMONIA YIELD, UNITS OF  $10^{17}$  MOLECULESTOTAL DOSE, UNITS OF  $10^{18}$  ev.

FIGURE XI

 $\gamma$ -Radiolysis of Methylamine

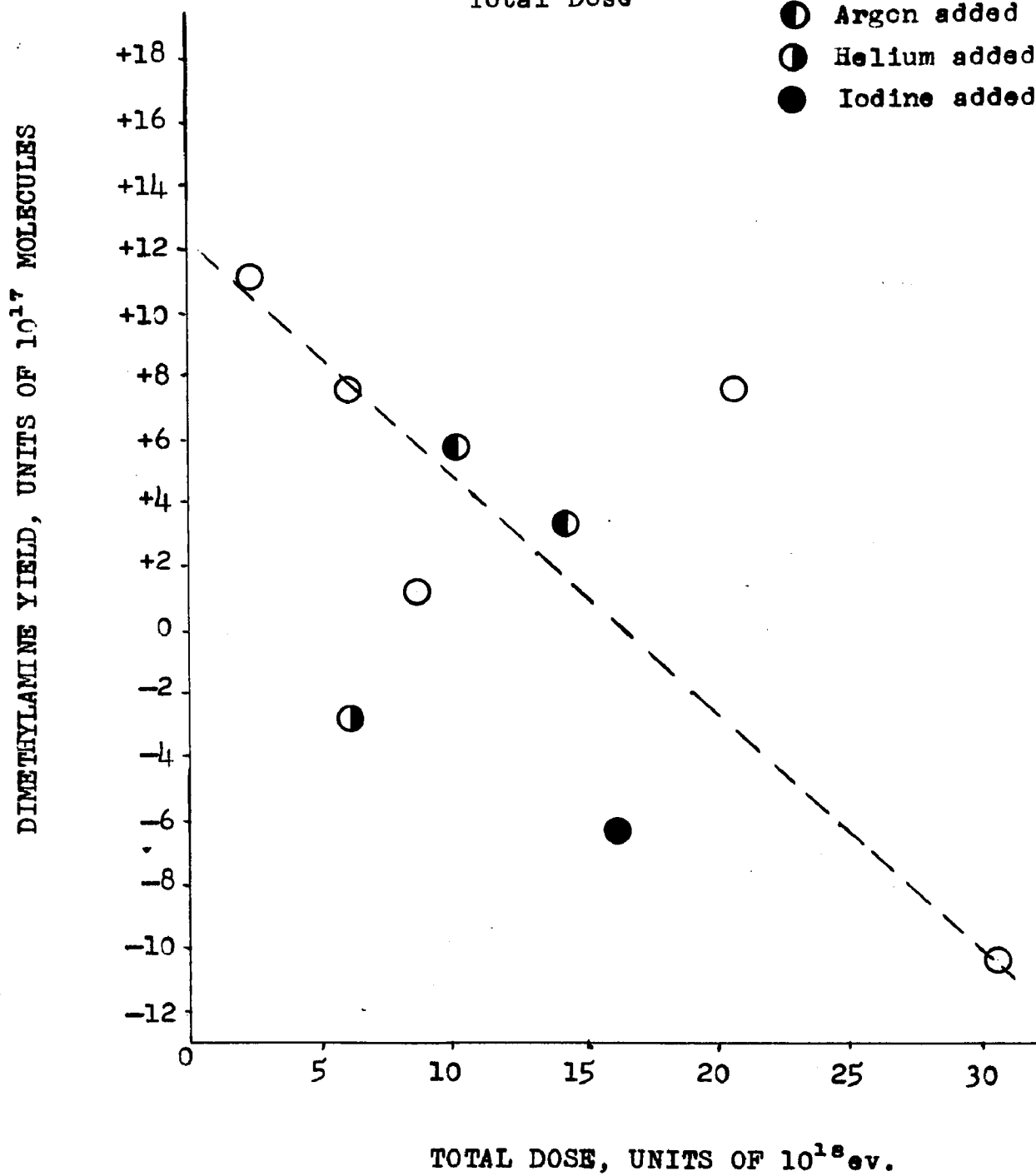
Yield of Dimethylamine

vs

Total Dose

Legend

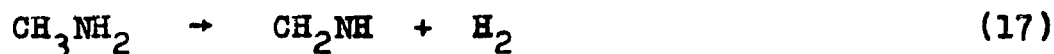
- Argon added
- ◐ Helium added
- Iodine added



$G_{H_2}^0 = 10.8$ ;  $G_{CH_4}^0 = 0.64$ ;  $G_{NH_3}^0 = 4.6$  and 10; the latter value for ammonia results from the higher initial concentration of methylamine. As seen from Figure XI, the dimethylamine reaches a high concentration, initially, and then decreases with irradiation time.  $G(-(CH_3)_2NH) = 7.44$ . This value was determined for the higher initial concentration of methylamine. Values were not obtained from samples containing, initially, a lower concentration of methylamine.

The yields of hydrogen and methane are independent of the initial pressure of methylamine in the region of 100 cm to  $\sim 274$  cm.

The formation of hydrogen can result from molecular elimination from methylamine.



Evidence for this comes from the photochemical study by Watson and Darwent<sup>15</sup> who found the 66% of the hydrogen formed from methylamine- $d_2$  was HD and 70% HD from methyl- $d_3$ -amine. Further proof for intramolecular detachment could be obtained from irradiations of mixtures of methylamine and methyl- $d_3$ -amine- $d_2$ .

All of the hydrogen may not be formed by reaction (17). Methylamine may dissociate via reaction (18),



the hydrogen atoms reacting to form hydrogen. ( $CH_4N^+$  is written in this manner since the actual structure of this ion is questionable.<sup>35</sup>)

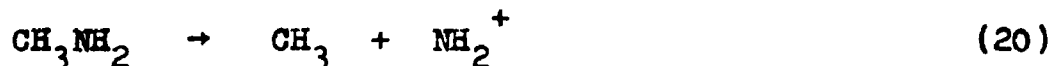
The addition of argon to methylamine ionization potential (8.97 v)<sup>6</sup>, shows no effect on the yield of hydrogen.

Methane formation may occur by several paths. Molecular elimination may occur via reaction (19).



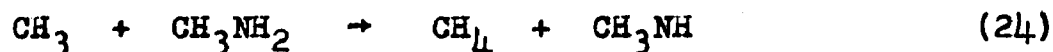
An isotopic study with deuterated and non-deuterated methylamine would indicate the importance of this reaction by obtaining the  $\text{CD}_4/\text{CD}_3\text{H}$  ratio.

Scission of the carbon-nitrogen bond under irradiation will result in both radical and ion formation via reactions (20), (21) and (22).



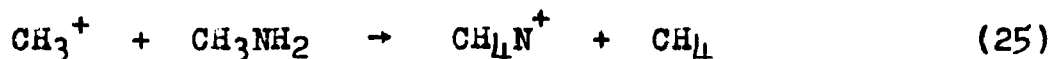
The mass spectral pattern of methylamine<sup>36</sup> shows that the relative abundances of  $\text{NH}_2^+$  and  $\text{CH}_3^+$  are about 15%. The methyl radical may then react with another methylradical forming ethane. Ethane was a product identified in the photolysis studies, but not detected in this study.

Methane can be formed by the methyl radical abstracting a hydrogen from methylamine.



Hydrogen abstraction by methyl radical from methylamine has been previously observed.<sup>37</sup> However, there exists doubt as to which hydrogen is abstracted.

Another reaction contributing to methane formation can be a hydride ion transfer reaction.

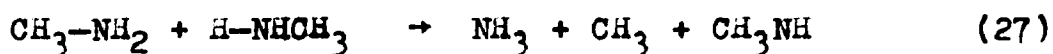
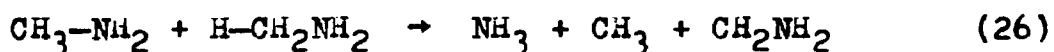


Hydride ion transfer reactions have been demonstrated in the mass spectrometer for hydrocarbon systems.<sup>38</sup>

Addition of argon shows a slight inhibiting effect on methane formation. Again the reason for this result is not well understood and it is suggested that more work with inert gases, at higher concentrations, be done before conclusive evaluations can be made. The inert gas may moderate some intermediate in such a way that methane formation is reduced.

As shown previously, hydrogen and methane formation are pressure independent, while the formation of ammonia is pressure dependent. Dimethylamine may also be pressure dependent, since the formation of these two products appear to be related.

The data definitely suggests a bimolecular reaction. Collision of two methylamine molecules via reactions (26) and (27) may result in formation of these products.

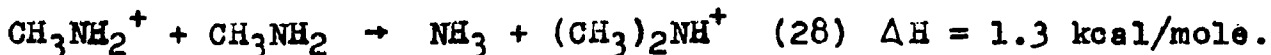


If the radicals are near thermal energies and in close proximity reaction (26) should lead to ethylamine, a product not observed. Reaction (27) can lead to dimethylamine.

It is unlikely that ammonia is produced from dimethylamine, since ammonia is not a product in the radiolysis of

dimethylamine.

An ion-molecule reaction may also be operative.



Observation of this reaction has not yet been reported.

Radical abstraction involving  $\text{NH}_2$  radical can also lead to ammonia.



Addition of iodine, a radical scavenger, resulted in a decrease in the yields of both ammonia and dimethylamine, 20% for ammonia and 22% for dimethylamine. These results indicate that radical reactions are in part responsible for these products.

Charge transfer reactions are demonstrated. The addition of helium and argon increase the yield of ammonia. The inert gases effect the excited states. Inert gas ions may also enter into ion-molecule reactions with methylamine as already shown with ammonia.

### C. Gamma Radiolysis of Dimethylamine

Hydrogen and methane were products identified from the radiolysis of dimethylamine. The presence of nitrogen, ammonia and trimethylamine were not indicated. Methylamine was tentatively identified as a product, when liquid was present in the irradiation tube. Consequently the methylamine may have been formed in a condensed phase reaction. Another sample, without liquid present, showed no methylamine formation. Both samples had been irradiated approximately

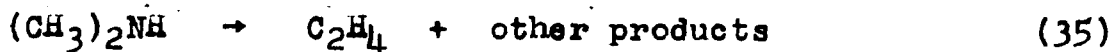
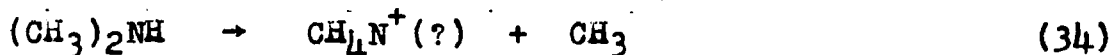
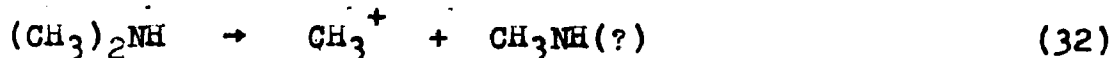
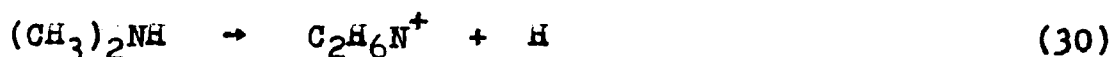
the same length of time.

Ethane, a photolysis product, and polymer formation were undetected.

The yields of hydrogen and methane are tabulated in Table 7. The initial G values are again taken from the initial slopes of the curves plotted in Figures XII and XIII.  $G_{H_2}^0 = 15$  and  $G_{CH_4}^0 = 2.9$ .

The addition of helium resulted in the increase of both hydrogen and methane. The ionization potential of dimethylamine is 8.24 v,<sup>6</sup> so that energy transfer from an inert gas ion can take place. A fortuitous result was the formation of  $4.25 \times 10^{17}$  molecules of trimethylamine.

Electron impact studies of dimethylamine<sup>35,39</sup> have shown the following reactions producing a variety of intermediate species.



These reactions account for the major mass peaks observed. The mechanisms or ion indicated by the question mark are not completely above suspicion.

Methyl radical can be formed via reaction (34). The methyl radical can then abstract a hydrogen from dimethylamine



TABLE 7

## Radiolysis of Dimethylamine

<u>Sample No.</u>	<u>Position in Source</u>	<u>Irradiation Time (minutes)</u>	<u>Total Dose ev x 10<sup>-18</sup></u>	<u>Initial Moles of (CH<sub>3</sub>)<sub>2</sub>NH x 10<sup>+4</sup></u>
15	6	9943	7.97	2.22
16	4	15530	16.5	2.39
19	5	20080	22.0	2.18
20	4	4550	4.43	2.18
22	6	10137	7.92	2.17
77	6	1625	1.24	2.12
45SHe*	8	10965	9.70	2.29

<u>Sample No.</u>	<u>Molecules of H<sub>2</sub> Formed x 10<sup>-17</sup></u>	<u>G<sub>H<sub>2</sub></sub></u>	<u>Molecules of CH<sub>4</sub> Formed x 10<sup>-18</sup></u>	<u>G<sub>CH<sub>4</sub></sub></u>
15	11.3	14.2	19.6	2.46
16	15.4	9.35	27.2	1.65
19	16.9	7.69	36.4	1.65
20	3.63	8.20	7.77	1.75
22	9.88	12.5	16.3	2.06
77	2.05	16.5	11.5	9.28
45SHe*	13.4	13.8	22.8	2.35

\*  $3.29 \times 10^{-6}$  moles of helium added (1.42 mole %) resulted in formation of  $4.25 \times 10^{17}$  molecules of trimethylamine

FIGURE XII

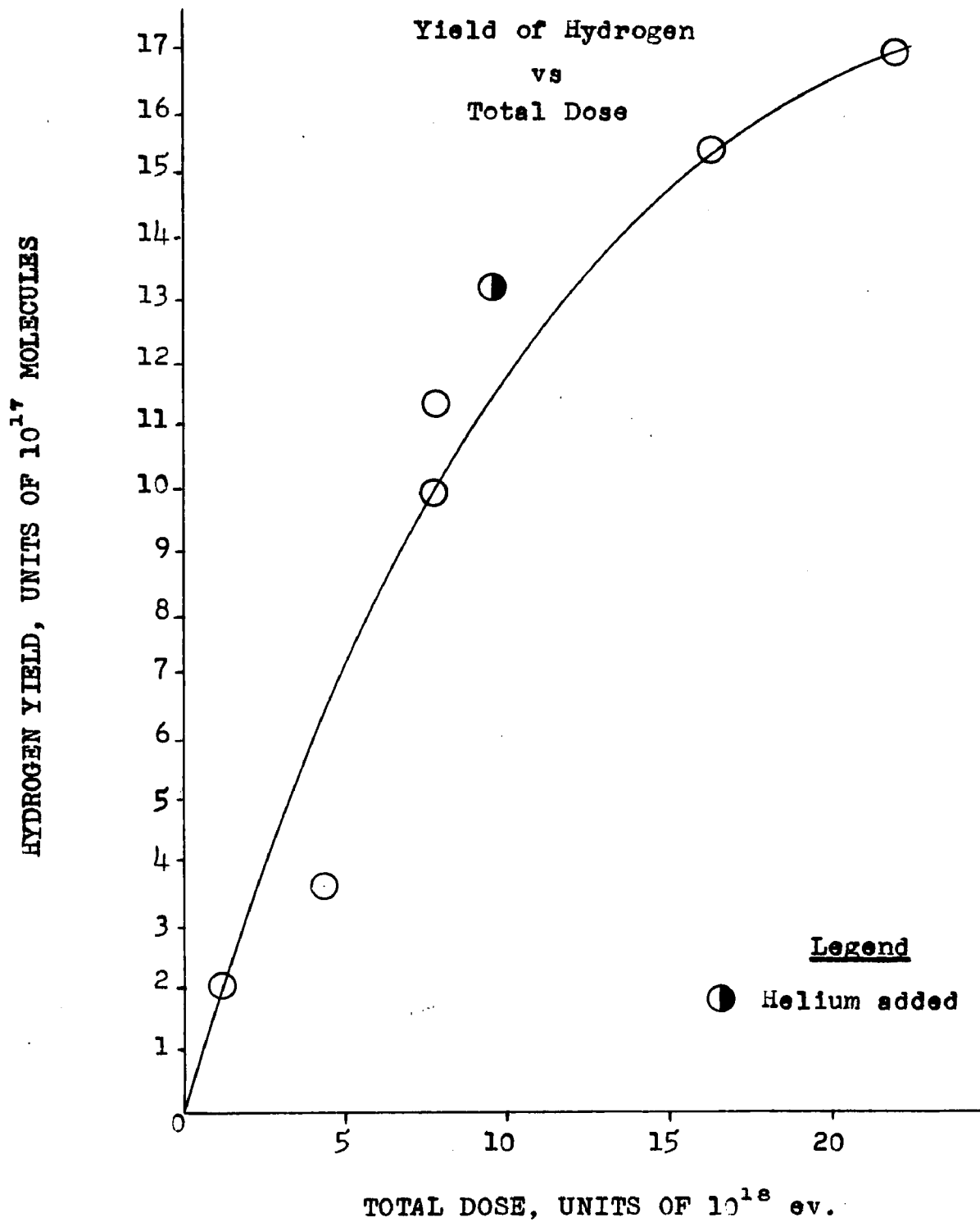
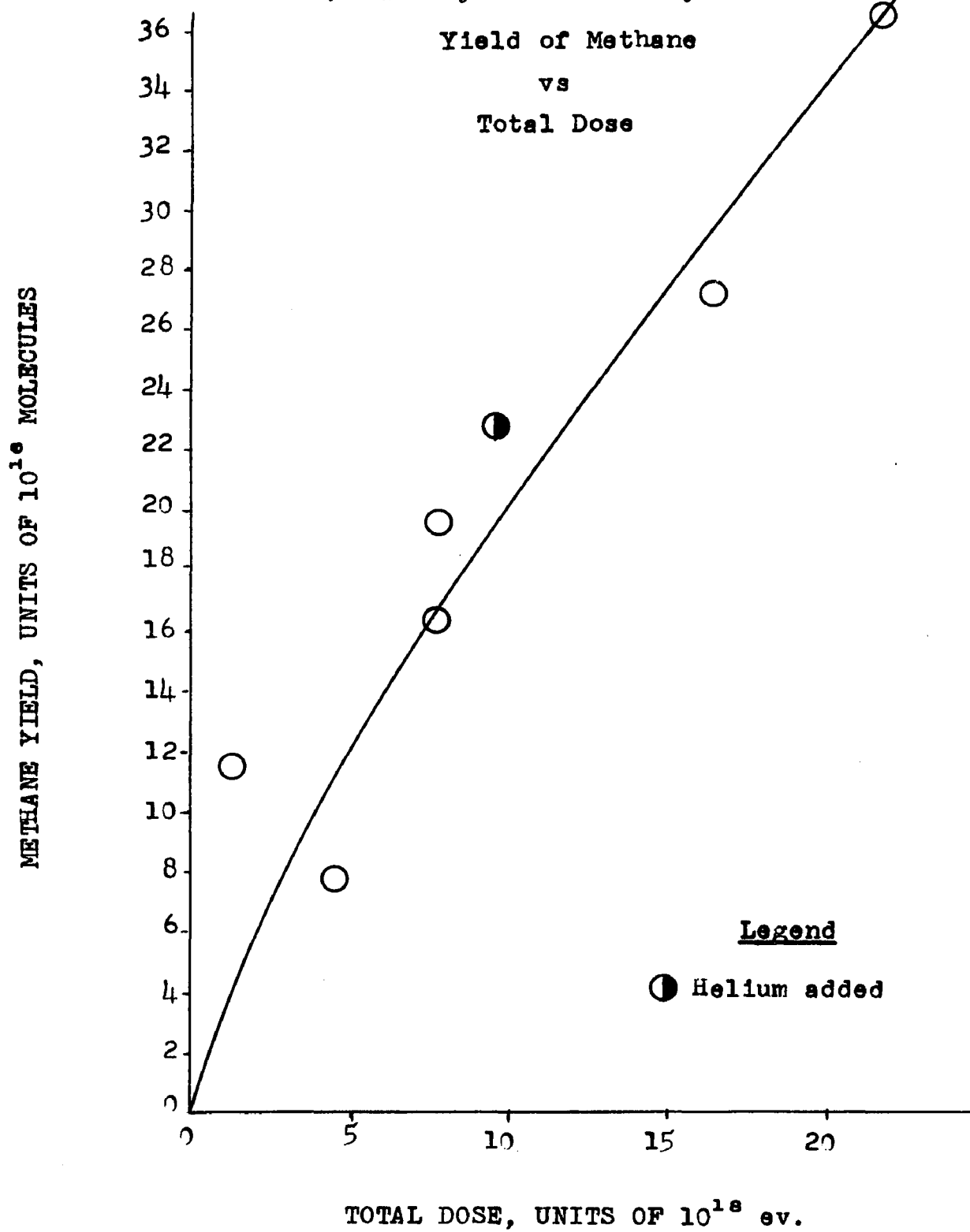
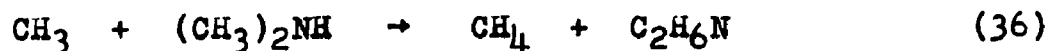
 $\gamma$ -Radiolysis of Dimethylamine

FIGURE XIII

$\gamma$ -Radiolysis of Dimethylamine  
Yield of Methane  
vs  
Total Dose



by reaction (36).<sup>37</sup>



Intramolecular elimination may explain, in part, both methane and hydrogen formation. Dissociation of an excited state or a molecule-ion of dimethylamine may also give these products. The contribution of these various processes is not known.

The fact that addition of helium resulted in trimethylamine formation shows that the excited state has been altered.

Accounting for the nitrogen balance has posed a problem. The nitrogen may well be contained in undetected products.

#### D. Gamma Radiolysis of Trimethylamine

The products from the radiolysis of trimethylamine are hydrogen, methane, dimethylethylamine and an unidentified compound. The original impurities, ammonia and another unidentified compound, were also increased due to irradiation. Nitrogen and methyl hydrazine were not observed. Liquid formation was absent.

The results are tabulated in Table 8. The peak height of the unidentified compound is listed as a measure of its concentration. Figures XIV and XV show the plotted results for hydrogen and methane.  $G_{\text{H}_2}^0 = 12.4$  and  $G_{\text{CH}_4}^0 = 2.63$  determined from the initial slopes of the curves. From the data on the unidentified compound, it appears to be formed initially in high yield. The formation decreases with in-

TABLE 8

## Radiolysis of Trimethylamine

<u>Sample No.</u>	<u>Position in Source</u>	<u>Irradiation Time (minutes)</u>	<u>Total Dose ev x 10<sup>-18</sup></u>	<u>Initial Moles of (CH<sub>3</sub>)<sub>3</sub>N x 10<sup>+4</sup></u>
36	2	6760	8.64	2.50
38	1	10965	13.7	2.53
39	3	18131	26.0	2.36
40	2	10841	13.0	2.34
42	1	6636	7.82	2.37
46SHe*	7	10841	13.4	2.24

<u>Sample No.</u>	<u>Molecules of H<sub>2</sub> Formed x 10<sup>-17</sup></u>	<u>G<sub>H<sub>2</sub></sub></u>	<u>Molecules of CH<sub>4</sub> Formed x 10<sup>-16</sup></u>	<u>G<sub>CH<sub>4</sub></sub></u>	<u>Peak Height of X</u>
36	6.32	7.32	21.6	2.50	N.D.
38	9.70	7.08	30.7	2.24	39
39	16.9	6.50	55.4	2.13	45
40	11.2	8.63	32.8	2.52	N.D.
42	8.85	11.3	21.7	2.78	61
46SHe*	13.8	10.3	40.9	3.05	28

\*  $3.96 \times 10^{-6}$  moles of helium added (1.74 mole %)

FIGURE XIV

 $\gamma$ -Radiolysis of Trimethylamine

Yield of Hydrogen

vs

Total Dose

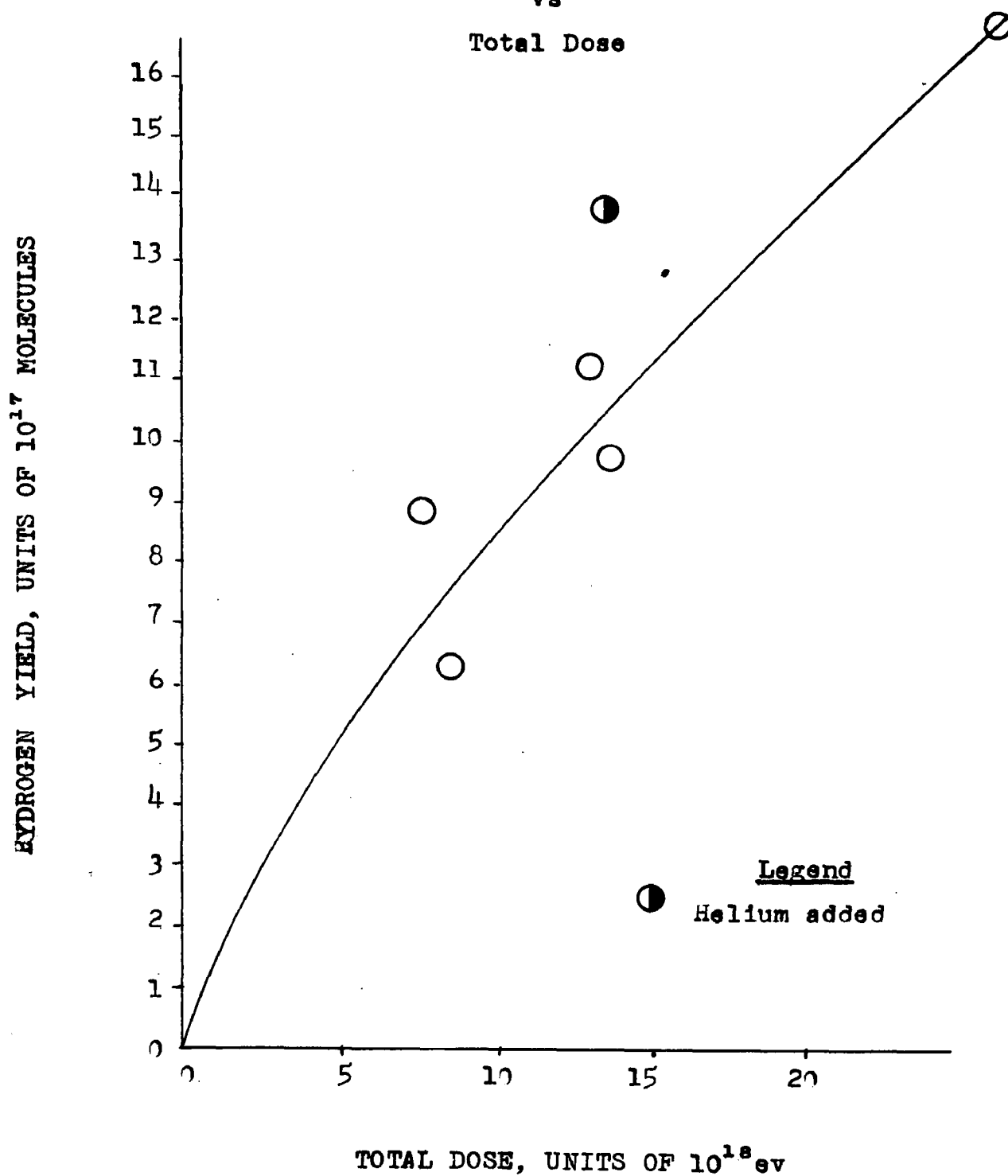


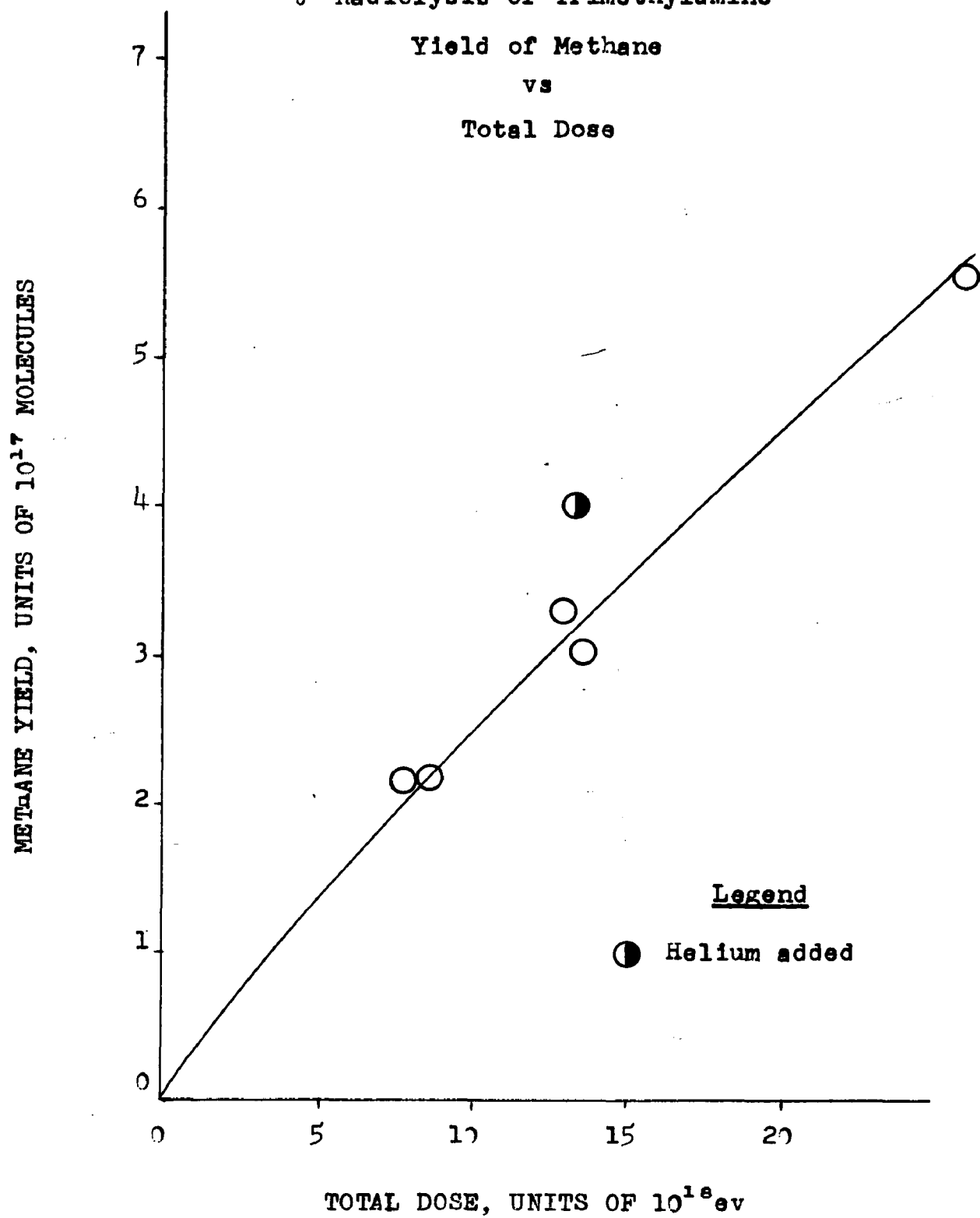
FIGURE XV

 $\gamma$ -Radiolysis of Trimethylamine

Yield of Methane

vs

Total Dose

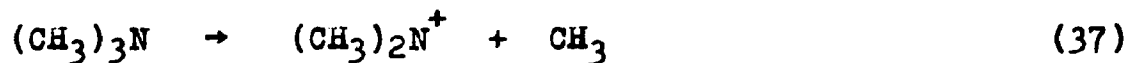


crease in irradiation time.

The addition of helium resulted in the enhancement of the hydrogen and methane and reduction of the unidentified compound. Addition of helium increased products, hydrogen and methane, in a previous photolysis study.

The predominate masses from electron impact studies of trimethylamine<sup>35,39</sup> are 15 ( $\text{CH}_3^+$ ), 42 (of ambiguous composition), 58 ( $\text{C}_3\text{H}_8\text{N}^+$ ), 59 ( $\text{C}_3\text{H}_9\text{N}^+$ ), 30 ( $\text{CH}_4\text{N}^+$ ), 28 ( $\text{CH}_2\text{N}^+$ ) and 44 ( $\text{C}_2\text{H}_6\text{N}^+$ ). The structure of masses 30 and 28 are questionable. The ion of mass 42 has a relative intensity of 46.3 for 70 volt ionization.<sup>39b</sup> The unidentified compound may be a consequence of a reaction involving this ion.

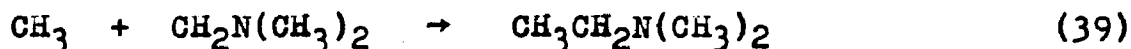
Methyl radical can be formed by the following reaction:



The methyl radical can then react with a hydrogen atom or abstract a hydrogen<sup>37a,c</sup> from trimethylamine.

Intramolecular elimination may contribute to the products. Other contributions may be from dissociation of excited states, dissociation of molecule-ions and ion-molecule reactions.

Dimethylethylamine may be formed by a two step mechanism involving radicals.



Ammonia formation may be involved in a complex reaction scheme.  $\text{NH}_4^+$  has been found in the mass spectrum.



Neutralization via reaction (6) will result in ammonia.  $\text{NH}_4^+$  also appears in the mass spectrum of dimethylamine, but ammonia was undetected as a product of its radiolysis.

#### E. Reaction of Nitrogen(II) Oxide with the Methylamines

Addition of nitrogen(II) oxide to the methylamines at liquid nitrogen temperature resulted in the formation of a white solid with each amine. The white solids decomposed rapidly on exposure to the atmosphere. These compounds were stable when sealed under excess amine.

The reaction of nitrogen(II) oxide with methylamine<sup>40</sup> and trimethylamine<sup>41</sup> has been previously reported.

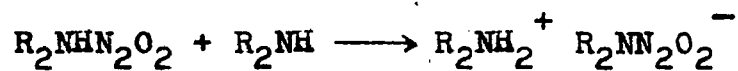
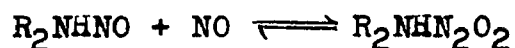
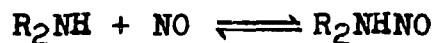
No elemental analysis was attempted on the solids obtained but from their behavior and appearance, it is felt that the compounds are those already prepared.

The method of preparation is different from that reported; these being prepared on the vacuum line by condensing a mixture of nitrogen(II) oxide and the amine at liquid nitrogen temperature.

The preparation of the dimethylamine compound is new. The probable compounds formed from the reaction are listed below.

Reaction	Compound
$\text{CH}_3\text{NH}_2 + \text{NO}$	$\text{CH}_3\text{NH}_3^+ \text{CH}_3\text{NHN}_2\text{O}_2^-$
$(\text{CH}_3)_2\text{NH} + \text{NO}$	$(\text{CH}_3)_2\text{NH}_2^+ (\text{CH}_3)_2\text{NN}_2\text{O}_2^-$
$(\text{CH}_3)_3\text{N} + \text{NO}$	$(\text{CH}_3)_3\text{NN}_2\text{O}_2$

The mechanism proposed for the reaction of the amine and nitrogen(II) oxide is the following:



The primary and secondary amines form ionic salts. Elemental analysis and infrared spectra of the stable compounds support this formulation. Trimethylamine is unable to undergo the third step in the mechanism, thus forming an addition compound.

## SUMMARY

Radiolysis of ammonia by cobalt 60 gamma rays resulted in hydrogen and nitrogen. The yield of hydrogen was observed over a seven fold change in total dose with an initial G value of 10. The presence of an inert gas shows charge transfer.

The radiolysis of methylamine resulted in hydrogen, methane, ammonia and dimethylamine as products. Hydrogen, methane and ammonia increase in yield with irradiation time. Dimethylamine is initially formed in high yield, then the yield decreases with irradiation time. Hydrogen and methane are pressure independent products. Ammonia and dimethylamine appear to be pressure dependent. Scavenger study with iodine indicates that ammonia and dimethylamine are partially produced by radical reactions. Charge transfer was again demonstrated with inert gases.

The initial G values were hydrogen, 10; methane, 0.64; and ammonia, 4.6 (  $\sim 100$  cm pressure  $\text{CH}_3\text{NH}_2$ ) and 10 (  $\sim 200$  cm pressure of  $\text{CH}_3\text{NH}_2$ ).

Hydrogen and methane were the only identified products from the radiolysis of dimethylamine. Both increase with irradiation time. The initial G value for hydrogen being 15 and for methane 2.9, the addition of helium resulted in formation of trimethylamine, and an increase in the yield of hydrogen and methane.

Hydrogen, methane, dimethylethylamine, ammonia and two unidentified compounds were formed from the gamma radiolysis of trimethylamine. Initial G values for hydrogen and methane were respectively 12.3 and 2.63. The presence of helium resulted in an increase in the yield of hydrogen and methane. One of the unidentified compounds decreased in yield with helium present.

Addition of nitrogen(II) oxide to the methylamines at liquid nitrogen temperature resulted in formation of white compounds. These compounds were unstable when exposed to the atmosphere. The dimethylamine compound has not been previously reported.

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## APPENDIX

<u>Sample No.</u>	<u>Measured Pressure (cm)</u>	<u>Measured<sup>22</sup> Volume (ml)+</u>	<u>Measured Temperature (°K.)+</u>	<u>Measured volume of irradiation tube (ml)<sup>22</sup></u>
9	2.71	291	302	4.40
11	2.49	291	300	4.67
13	2.58	291	298	3.76
15	1.45	285	297	3.99
16	1.55	285	296	3.79
19	1.43	285	298	4.45
20	1.43	285	299	4.19
22	1.42	285	298	3.62
24	1.34	285	298	4.47
30	1.50	285	302	3.83
31	1.39	285	302	3.92
32	1.60	285	302	3.67
33	1.60	285	302	4.00
34	1.60	284	300	3.97
36	1.65	285	302	4.07
38	1.57	285	302	4.10
39	1.56	285	303	3.58
40	1.56	285	303	3.90
42	1.57	285	302.	4.05
58	4.46	174	298	3.80
59	4.42	174	298	3.44
60	4.58	174	298	3.59
63	2.73	174	296	4.09



<u>Sample No.</u>	<u>Measured Pressure (cm)</u>	<u>Measured<sup>†</sup> Volume (ml)+</u>	<u>Measured Temperature (°K.)+</u>	<u>Measured volume of irradiation tube (ml)<sup>‡</sup></u>
65	2.73	174	296	3.77
66	2.57	174	296	3.51
68	2.82	174	300	3.58
69	2.82	174	300	3.86
71	2.80	174	299	3.95
77	2.25	173	296	3.50
78	4.54	174	297	2.88
43SHe	1.57	285	301	4.18
44SHe	1.54	285	301	3.92
45SHe	1.50	285	299	4.15
46SHe	1.47	285	299	4.39
50SAr	2.74	174	298	3.76
51SAr	2.88	174	299	4.33
52SAr	2.94	174	299	3.93
53SAr	2.93	174	299	3.57
61SI <sub>2</sub>	4.43	174	296	3.51

<sup>†</sup> rounded off to nearest whole number.

<sup>‡</sup> does not include volume of break seal, which varied in volume from 0.1 to 0.2 ml. (average 0.13 ml.)

## BIOGRAPHICAL DATA

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Date of Birth	August 24, 1935	
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Secondary Education	Stuyvesant High School, New York City	
Collegiate institutions attended	Dates	Degree
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## Publications:

Amell, A. R., Lamprey, P. S., and Schiek, R. C.,  
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